DESALINATION TECHNOLOGIES AND ENVIRONMENTAL ASPECTS: CASE STUDY IN LIBYA

By

ALI HASSIN SALEH EL-HAJAJI

A thesis submitted in fulfilment of the requirements of Liverpool John Moores University for the degree of

Doctor of Philosophy

November 2017

Abstract

Water, otherwise known as the pool of life, is the very essence of all living things and as such is vital for survival, whether for living beings, social, economic development or for environmental sustainability. However, its continuing existence is severely threatened for future as a result of climate change, carbon footprint, population growth, environmental damage, combined with natural disasters like droughts and floods. The prospect of an alternative solution such as desalination of sea or brackish water to counter the limit on conventional water resources such as groundwater, which cannot meet demand, is therefore very promising, particularly in arid and semi-arid regions where water scarcity and impaired quality prevails. Consequently, desalination technology has now become a burgeoning industry in North Africa or southern Mediterranean countries, such as in Libya. However, evidence suggests that as a result of by-products being discharged directly into the sea, particularly from coastal desalination plants, the physico-chemical parameters of the receiving water are changing and posing a threat to marine ecosystems. As a result of studies conducted on these parameters to analyse the brine emitted from the Zwuarah and the West Tripoli distillation plants (ZWDP & WTRIS) on the Libyan coastline, evidence shows there is a significant positive correlation at both sites between the biological data and physico-chemical parameters ($\boldsymbol{r_s}$=0.673; p=0.002) and ($\boldsymbol{r_s}$=0.637; p=0.003), which is a clear indication of the impact of brine disposal from both plants on the marine environment.

For most of coastal desalination plants on the Libyan coastline, the most practical and least expensive brine disposal option is to discharge it into the sea. It is necessary therefore, to effectively manage desalination reject brine in order to ensure more efficient disposal and reuse. Therefore, it is suggested that experimental studies are aimed for dual benefit of on-site generation of sodium hypochlorite through brine electrolysis and to recover minerals and NaCl from the brine using evaporation ponds, while protecting the environment. Following the first experiment, the outcome of brine utilisation showed a significant production of NaOCl using graphite electrodes (MCCA 1.82 gr/m^3). At interelectrode spacing 2 cm and 4 cm, the power consumption was higher, with a greater concentration of sodium hypochlorite generation varying between 10-25 kw/m3 (573-2140ppm) and 29-24 kwm^{-3} (572-2600ppm) than at

interelectrode spacing 6cm 17-13 kwm^{-3} (350-1790ppm). Consequently, the selection of an optimum electrical consumption level is key in establishing the best scenario in terms of economy and efficiency. Subsequent to the second experiment of brine evaporation in the ponds, results showed that the evaporation rate in August was lower than in September (9.06 $mmday^{-1}$, 14.63 $mmday^{-1}$) respectively. The results of the SEM/EDS test showed that due to elevated surges of Na^{+} and Cl^{-}, halite (NaCl) was the main mineral evident during crystallisation of the salt samples. Hence, the two experiments reveal that brine can be recycled productively, while protecting the environment.

Declaration

I, Ali Hassin Saleh El-Hajaji, declare that this thesis, submitted in fulfilment of the requirements for award of Doctor of Philosophy, in the school of Civil Engineering, Liverpool Johan Moores University, is my own work, except where otherwise referenced or acknowledged. This thesis was completed under the supervision of Prof. Rafid Al Khaddar, Dr. Simone Dürr and Dr. Daw Haddoud, and has not been submitted for qualification at any other academic institution.

Ali Hassin Saleh El-Hajaji

November 2017

Acknowledgements

I would like to express my sincere gratitude to my wonderful supervision team (Prof. Rafid Al Khaddar, Dr. Simone Dürr and Dr. Daw Haddoud and the advisor Prof. David Phipps) for their invaluable guidance and great patience during the course of this study. This would not have been possible to achieve without their academic and moral support through hard times.

I also would like to thank the laboratory technical staff in the School of Civil Engineering at Liverpool John Moores University, especially Mr. Malcolm Freegan and Mr Hewitt David. I should also thank the General Desalination Company of Libya and Marine Research Centre, Tajura/Tripoli for the laboratory tools that they provided to complete my research.

The contributions of engineer Sammy Zawgyi (Head of Chemical Department at Zwuarah Desalination Company in Libya) and Dr. Daw Haddoud (Head of Marine Research Centre, Tajura/Tripoli) cannot over-emphasised. Eng. Sammy used his wealth of knowledge and experience in order to install the evaporation ponds close to Zwuarah Desalination station, while Dr. Daw Haddoud also used his expertise and skill regarding the marine data collection.

I should also thank the Ministry of Higher Education and Scientific Research of Libya and Libyan Cultural Affairs in London for their sponsorship and financial help. Also, I am thankful to my lovely friends and colleagues, namely Caroline Helal and Amhmed Bhih for their encouragement and moral support.

This project would not have been completed without the support of my great family, especially my brother Adnan for his continuous support during the course of my study.

GOD BLESS YOU ALL!

Dedication

This thesis is dedicated specially to:

Allah, the most Gracious and the most Merciful

Prophet Mohammed (May Allah bless him) and his household

My parents for making my research work possible and their continued prayers, moral and financial support who have spent their lives raising seven children to see them as teachers, dentist, and doctors.

My best brother Adnan and my five sisters for their support.

My beloved wife for her endless love, patience, encouragement and support.

My beloved son Al Hussain who makes the world a much happier place.

My Father-in-law Mohamed Shamaka for his continuing support.

GOD BLESS YOU ALL! AND THANKS FOR THEIR LOVE, SUPPORT AND ENCOURAGEMENT TO MAKE THE DREAM REALISED

Scientific contributions arising from this PhD work

Elhajaji, A and Al Khaddar, R. (2017) Salt production by the evaporation ponds of brine disposed from distillation plant. Full paper, *Faculty Research Week 2017*, Liverpool John Moores University, 22nd May, 2017.

Elhajaji, A and Al Khaddar, R. (2016) Produce Sodium Hypochlorite on site from the brine disposed of thermal desalination plants: Libya's case study Full paper, Faculty Research Week 2016, Liverpool John Moores University, 18th April, 2016.

Elhajaji, A., Al Khaddar, R., Haddoud, D., and Dürr, S. (2015) The Impact of Thermal Desalination Technologies MED with TVC and without TVC on the Libyan Coastline (WEWRC: May 2015) , World Environmental and Water Resources Congress 2015: pp. 2480-2492: doi: 10.1061/9780784479162.243: paper expected and published at: http://ascelibrary.org/doi/abs/10.1061/9780784479162.243

Elhajaji, A., Al Khaddar, R., Haddoud, D., and Dürr, S. (2014) Thermal Desalination Technologies as An alternative Option of Water Scarcity in Libya (WEWRC:1-5 Jun 2014), *World Environmental and Water Resources Congress 2014*: pp. 2247-2258:doi: 10.1061/9780784413548.224) (Oral presentation) paper expected and published at: http://ascelibrary.org/doi/abs/10.1061/9780784413548.224

Elhajaji, A., Al Khaddar, R., Haddoud, D., and Dürr, S. (2014) Physicochemical impact of brine discarded from thermal desalination plants on marine communities: Case Study-Libya, *9th Annual Bean Conference Proceedings*, Liverpool John Moores University, 18th Jun, 2014.

Elhajaji, A., Al Khaddar, R. (2013) Minimizing the negative impact of thermal seawater desalination plants by matching MED and solar distiller-Case study Libya – Part -1, *8th Annual Bean Conference Proceedings*, Liverpool John Moores University, 18th Jun, 2013.

Contents

List of figures and tables

List of symbols and abbreviations

$	USA dollar
$/ha	Dollar per hectare
$/m^3	USA dollar per cubic metre
^{0}C	Celsius
^{0}F	Fahrenheit
A	Pond open surface area
acre	Land area
Ae	Evaporative area
ANOSIM	Analysis of similarities
A_t	Total area required (acres)
Br^-	Bromide
Br_2	Bromine
BWRO	Brackish water
Ca^{2+}	Calcium ion
$CaCO_3$	Calcium carbonate
$CaCO_3$	Total alkalinity
$CaCO_3$	Total Hardness as $CaCO_3$
$CaCO_3$	Calcium Hardness as $CaCO_3$
$CaCO_3$	Magnesium Hardness as $CaCO_3$
Cc	Land clearing cost
$CHBr_2Cl$	Dibromochloromethane
$CHBr_3$	Bromoform
Cl^-	Chloride ion
Cl_2	Chlorine
cm	A centimetre
CO	carbon monoxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate
Cu^{2+}	Copper
D	Minimum pond depth
DC	Direct current
DIC	Dissolved inorganic carbon
d_{min}	Minimum depth
DPD	Chlorine Reagent Powder Pillow
DSA	Dimensionally stable anode
E	Energy consumption
ED	Electrodialysis
EDM	Electrodialysis metathesis
EDR	Electrodialysis Reversal
EDX	Energy-dispersive X-ray spectroscopy
ER	Electrodialysis Reversal
es & e	Saturation vapour pressure of water and ambient water vapour pressure
F (u)	Wind speed
F_1	Empirical safety factor
Fe^{2-}	Ferrous ion
$FeCl_3$	Ferric chloride

$FeSO_4$	Ferric sulphate
ft	Feet
g/l	A gram per litre
GDCOL	General Desalination Company of Libya
GEA	General Environment Authority
GECOL	Electricity and Renewable Energy Authority
GMMR	Great Man-made River Project
gr/m^3	Gram per cubic metre
GWA	General Water Authority
GWSCo	General Water and Sanitation Company
H	Hectares
H^+	Hydrogen
H_2	Hydrogen
H_2CO_3	Carbonic acid
H_2SO_4	Sulphuric acid
HCO_3^-	Bicarbonate ion
HERO™	High Efficiency reverse osmosis
HFF	hollow fine fibre
HOCl	Hypochlorous acid
Hr	Daily average of the relative humidity
IPCC	Intergovernmental Panel on Climate Change
J	Current density
K^+	Potassium
KG	Sediment kurtosis
km	kilometre
km^3/year	Cubic kilometre per year
kPa	kilopascal
kPa $°C^{-1}$	Kilopascal per Celsius
kV	Kilovolts
kW h	kilowatt hour
kW h/m^3	kilowatt hour per cubic metre
l/m^2/day	litres per square per day
LBSC	Libyan Bureau of Statistics and Census
Lc	Land cost
LCV	Lower convective zone
M	Metre
M km^3	Million cubic kilometre
M m^3	million cubic metre
M m^3 $year^{-1}$	Million cubic metre per year
m^3	A cubic metre
m^3/day	A cubic metre per day
mA/cm^2	Milliampere per square centimetre
MCr	Membrane Crystallisation
MD	Membrane Distillation
MED	Multiple-Effect Evaporation
MED-TVC	Multiple-Effect Evaporation with Thermal vapour compression
MF	Microfiltration
$Mg(OH)_2$	Magnesium hydroxide
mg/l	milligrams per litre

µg/l	Microgram per litre
µS/cm	Micro Siemens per centimetre
Mg^{2+}	Magnesium
MGD	Million gallons per day
MGZ	Main gradient zone
MJ m^{-2} day^{-1}	Megajoule per square metre per day
MJ/m^3	Megajoules per cubic metre
MJkg-1	Megajoule per kilogram
mm	Millimetre
Mm^3/day	Million a cubic metre per day
$mmday^{-1}$	Millimetres per day
ms^{-1}	Metre per second
MSF	Multi-Stage Flash distillation
MVC	Mechanical vapour compression
Mz	Mean grain size
N_2H_4	Hydrazine
Na^+	Sodium ion
Na_2SO_3	Sodium sulphite
NaCl	Halite
$NaHSO_3$	Sodium bisulphite
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NF	Nano filtration
nMDS	Non-metric multidimensional scaling
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
NOC	National Oil Corporation Authority
NOx	nitrogen oxides
NPP	Net primary productivity
NVC	Non-convective zone
OH^-	Hydroxyl
P	Power consumption
PCA	Principle component analysis
PCM	Phase change material
PGR	population growth rate
pH	Acidity or alkalinity of a solution on a logarithmic scale
PO_4^{3-}	Phosphorus total
ppm	Part per million
psu	Practical Salinity Unit
Q	Average solar radiation
R	Global test
Rn	Net radiation
RO	Reverse Osmosis
r_s	Spearman rank correlation coefficient
SAL-PROC	Salt Recovery Salt Solidification and Sequestration
SEM	scanning electron microscopy
SIMPER	Average similarity, dissimilarity and abundance marine species
Skewness	SKI

SO_2	Sulphur dioxide
SO_4^{--}	Sulphate
SWRO	Seawater reverse osmosis
T	The time in hours
T	Average of the daily maximum and minimum temperatures recorded at the site
T	period of time between population number in the second census and the population number in the first census
TDS	Total dissolved solids
THM	Trihalomethanes
t_l	Liner thickness
TVC	Thermal vapour compression
U	The total electric voltage
U_2	Average of the daily maximum and minimum wind speed
UCV	Upper convective zone
UF	Ultrafiltration
V	Volume of reject brine
V past	population number in the first census
V present	population number in the second census
VC	Vapour Compression Evaporation
WAIV	Wind Aided Intensified Evaporation
WFD	Water Frame Work Directives
WHO	World Health Organization
WK1	Manganese reagent
WK2	Alkaline-iodide reagent
Wm^{-2}	watt per square metre
wt%	Weight percentage
WTRIS	West Tripoli distillation plant
ZLD	Zero liquid Discharge
ZWDP	Zwuarah distillation plant
Γ	Psychrometric constant
Δ	Saturation vapour pressure
δI	Standard Deviation
Λ	Latent heat of vaporization

Chapter One : Introduction

1.1. Research Overview

The United Nations made a declaration in 2010 regarding the necessity of a stable drinking water supply as a basic human right, to highlight the major issue of insufficient water quantity or quality (Pinto and Marques, 2017). Existing watercourses have long been the source for domestic, commercial, agricultural and urban use (Foster, 2001). Hence, the study of water quantification has been high on the agenda of professionals in the field of hydrology (Milano et al., 2013).

Over the past few decades, the intensity and acceleration of global warming has sparked serious concern (Frich et al., 2002; (Barnett et al., 2001). Following a huge convention of 20 research groups selected by the Intergovernmental Panel on Climate Change (IPCC) as part of its Fourth Assessment Report, simulations of anticipated scenarios using varying levels of greenhouse emissions, were set up to illustrate predictions in the 20th and 21st centuries. These proved that the raised level of industrial activity contributed to elevated emissions leading to climate change which ultimately influences water resources and supply (Milano et al., 2013).

According to the Council of Europe (2012), the Mediterranean basin is defined as being the most susceptible to climate change, due to anthropogenic activity. It has been predicted that by 2050, due to climate change, the existing severe water stress experienced in the southern and eastern regions of the Mediterranean basis will extend right across the basin, due to a 30-50% drop in freshwater sources and twice the amount of water consumption in the area (Viola et al., 2014). As the demand for water significantly increases from residential, industrial and agricultural sectors globally (Tal, 2006), there is a lack of sustainability to match the need (Barron et al., 2015). which has prompted the necessity to find alternative water sources. Hence, desalination has now become an option to meet this global surge of demand and will eventually become a solution for economic, social and environmental development Medeazza, 2005; Tsiourtis, 2001) while protecting water sources and maintaining environmental equilibrium (Bargues, 2014).

There are two types of commercial desalination technologies, namely thermal distillation, i.e. multi-stage flash distillation (MSF) or multiple-effect distillation (MED) or multiple-effect distillation with thermal vapour compression (MED-TVC) which are used in medium and large sized plants. The other technology is membrane separation known as reverse osmosis (RO) which is used in smaller plants (Mezher et al., 2011; Tsiourtis, 2001; Bargues, 2014). In addition, there are hybrid techniques using both technologies (Hamed, 2005). Also, there are smaller commercial desalination units divided into vapour compression (VC) and solar distillation. Other technologies include electro dialysis (ED) and electro dialysis reversal (EDR) which are used on a smaller scale, with minimal salinity (Khawaji et al., 2008; Schenkeveld et al., 2004). Further developments still under research are evolving, such as membrane distillation (MD) (Belessiotis et al., 2016), forward osmosis (FO), capacitance deionization (CDI), and gas hydrates (GH), freezing, humidification and dehumidification (HDH). Other supporting technologies include ultra/nano/ionic filtration (UF/NF/IF respectively) (Mezher et al., 2011; Cipollina et al., 2009; Krishna, 2004).

Thermal techniques are currently used in the Gulf and North Africa such as Libya Khordagui,2013; Elabbarb and Elmabrouka, 2005) where energy sources are abundant, while membrane techniques such as RO is more popular in developed countries for effective scale of economy (Bargues, 2014). As a sub-Saharan nation, over 80% of the population of Libya is located along the length of the coastline where agriculture and industry thrives due to arable land and favourable conditions (Kershman, 2001; Abufayed and El-Ghuel, 2001) There are 3,500 hours of sunlight annually, radiation on a horizontal plane is 7.1 $kwhm^{-2}day^{-1}$ in the coastal areas with 8.1 $kwhm^{-2}day^{-1}$ in the southern region, causing long term drought. (Saleh, 2006). Owing to an exceedingly hot and dry climate with temperatures reaching 40°C, evaporation rates are one of the highest globally (Abufayed and El-Ghuel, 2001). Potable, industrial and irrigation water originates from groundwater as the main source. However, for more than 20 years, demands on groundwater from different sectors has resulted in falling water levels and impaired quality, exacerbated by an influx of seawater along the coast (Sadeg and Karahanoðlu, 2001). Hence the drive to search for alternative water sources such as water desalination, large water transfer

(Great Man-made River Project), and wastewater recycling and reuse (General Water Authority, 2004).

In Libya, exploitation of oil uses desalination technology in arid regions where there is limited water supply, making Libya the largest user of thermal and membrane technology in North Africa and the Mediterranean region (Abufayed and El-Ghuel, 2001; Kershman, 2001). Desalination optimises the use of available resources such as saline or brackish natural water sources to produce freshwater (Eslamian, 2016). It has become a favourable alternative method due to inflation of water production costs and subsequent improved cost-saving technology (Barron et al., 2015). A large majority of the more substantial plants are run and managed by the General Electricity Company of Libya (GECOL) (Kershman, 2001) and General Desalination Company of Libya (GDCOL) (General Desalination Company of Libya, 2013) in addition to smaller and high capacity plants that use membrane and thermal techniques (run by major oil companies. Al-Hengari et al., 2015). Plans are in place to expand the capacity of thermal desalination plants along the Libyan coast in addition to the installation of a new one to support the existing somewhat inaccessible Great Man made River System (Elabbar, 2008; Elabbarb and Elmabrouka, 2005; Elhassadi, 2013).

There are massive implications of the desalination process in terms of environmental and ecological damage (Dupavillon and Gillanders, 2009), which need to be considered, such as energy and land usage, toxic emissions and brine discharge during regular operation. The latter has the most devastating impact (Bleninger and Jirka, 2008, Bleninger et al., 2010), coastal desalination plants continuously discharge by-products (brine) which have a major effect on the marine environment (Frank et al., 2017). This rejected brine is characterised by varying concentrations of salts and minerals including $SO4^{2-}$, Cl^{-}, Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}, Fe^{2-} and Cu^{2+} depending on feedwater quality, type and recovery percentage of the desalination process as well as any chemical additives used (Abdulsalam et al., 2016; Hu, 2014). Brine waste generated from coastal desalination plants has double the salinity of the receiving environment and is very concentrated causing it to sink onto the seafloor where it flows as a dense stream (Bleninger et al., 2010; Arafat, 2017; Torquemada et al., 2005). As it lengthens along the seafloor, (Frank et al., 2017) it intensifies in temperature, chemicals and salinity thus affecting water quality, causing damage to

marine biodiversity, flora and fauna and key components of coastal ecosystems (Lattemann and Höpner, 2008). Another problem is caused by the corrosion phenomenon within the desalination process where a combination of metals such as (copper, nickel, iron, chromium, zinc etc.) released with the brine may also pose an environmental threat (Giwa et al., 2017).

There is a public misconception that brine waste does not affect marine life (Ahmad and Baddour, 2014). In fact, there is no evidence of objection from local communities about the effects of brine discharge (Torquemada and Lizaso, 2005). However, research indicates adverse impact on echinoderms and bivalves as well as seagrasses and macroalgae (Castriota et al., 2001). In large-scale desalination plants, it is frequently conveyed via diffuser systems away from the shore or by direct beach discharge mixed with cooling water from nearby power plants (Fritzmann et al., 2007; Lattemann and Höpner, 2008).

Brine management techniques include brine minimization, direct disposal or reuse. The former applies membrane/thermal based, and emerging technologies still under development. Direct disposal options involve inland and offshore disposal techniques (Giwa et al., 2017). Inland desalination plants tend to incur higher disposal costs of brine than coastal plants, depending on characteristics of brine concentration, volume and concentration, treatment levels prior to discharge and disposal method (Arnal et al., 2005). There are several options for direct disposal of desalination into the sea, namely the use of evaporation ponds or shallow basins that are exposed to the open air, decreasing the amount of discharge (Rodríguez et al., 2012). This method is particularly effective in dry, warm locations with high evaporation rates and low land costs. Recently, there has not been much publicity about the use of brine disposal from desalination plants as opposed to the conventional use of seawater in salt work (Ahmed et al., 2000; Cipollina et al., 2012; Rodríguez et al., 2012). Thus, Libya has been chosen as a case study for considering the environmental impact of brine disposal from thermal desalination plants (MED, MED-TVC) on the Libyan coastline. Therefore, the following questions will be asked as outlined:

- What are the physico-chemical effects of brine influx from thermal desalination plants on the Libyan coastline?

- What strategies can be put in place for Libya to capitalise brine disposal in the form of minerals and salt?

These questions are behind the performance of this study and its results will provide the answers. This chapter presents research aims and objectives, novelty of research, the benefits and its impact, research sources and the thesis outline.

1.2. Research aims and objectives

The main aim of this thesis is to determine the physico-chemical effects of brine influx from thermal desalination plants on the receiving water in addition to evaluating the impact on the marine ecosystems. Further to this aim, this study is **to** look at the possibility of exploiting brine production by recycling it in the form of sodium hypochlorite, minerals and NaCl (halite).

This leads to the following specific objectives:

1. To evaluate and review existing global desalination techniques, including the chemicals that are used and their environmental impact.

2. To identify and evaluate different brine disposal methods used globally, water availability and regional desalination techniques, to understand Mediterranean legislation and how it can be relevant to brine management in Libya.

3. To assess existing water sources in Libya and ascertain suitable desalination technology by using one of the existing desalination plants on the Libyan coastline as a case study.

4. To examine the environmental impact of brine disposal from desalination techniques, using the Libyan coastline as a case study, investigating the relationship between the physico-chemical parameters of brine disposed and marine species.

5. To look at the potential of recycling brine disposed from Libyan coastal desalination plants using electrochemical and evaporation pond techniques to produce sodium hypochlorite, minerals and NaCl (halite).

1.3. Novelty of research

The innovative aspect of the current research work project can be summarised in the following:

- Although seawater desalination plants have been operating in various regions, there is very little data available about the ecological impacts of the brine on the marine environment (National Research Council, 2008). When any new project is embarked on, environmental impact assessment (EIA) study is the best means of recognising, evaluating and preventing ongoing damage to the environment, but no in-depth study has been carried out for desalination plants which would be very desirable (Lattemann, 2010). Little has been done in this area. The majority of analysis in Libya has focussed on the effects of increasing seawater salinity at the intake and their impact on the components of the desalination units, such as boilers and vulnerable instruments (Elabbarb and Elmabrouka, 2005; Brika et al., 2016). There is yet to be any research done regarding the ecological impact of brine disposal from thermal desalination plants in Libya. Hence, the novelty of this study and the knowledge gleaned from the research completed to determine the physico-chemical composition of brine, contributes to the validity and importance of this study when assessing the environmental implications of brine on the marine ecosystems.

- Most desalination plants, whether thermal distillation or reverse osmosis, are normally constructed with a hypochlorination unit, which produces sodium hypochlorite through seawater electrolysis for the purposes of injecting it at the seawater intake to prevent ongoing biological fouling in the desalination pipes and instruments while extending the longevity of the plant (Ozair and Al-Shangiti, 2013). A few basic experiments have been carried out to test the production of onsite sodium hypochlorite (NaOCl) through brine electrolysis (Wahab and Al-Weshahi, 2009). This paves the way for an innovative method to discuss various critical operating parameters for onsite sodium hypochlorite (NaOCl) production using an electrochemical cell in controlled conditions fed by the brine disposal from a thermal desalination plant.

- One area of concern is the high volume of concentrated brine disposed directly into the sea from desalination plants (Cipollina, 2012). Hence, the use of evaporation ponds offers a favourable alternative for brine disposal (Rodríguez et al., 2012) particularly where evaporation rates are high and accessibility of land near the coastal area is plentiful and economic. The integrated production of fresh water and recycled brine from desalinations plants could be achieved by utilising the brine disposal from thermal desalination plants as a feed for conventional salt works with the advantages of higher temperatures of brine, thereby speeding up the evaporation rates on the pond surfaces. Very little data exists about this concept other than studies completed in Tripani/Italy and Eilat/Israel (Ravizky, 2007; Cipollina, 2012). As a result of a warm, dry climate along the Libyan coastline with an abundance of sunshine, and plenty of land that is not over priced, there is a real opportunity to capitalise on these favourable conditions. Therefore, the final contribution of this research advocates the use of evaporation ponds as opposed to traditional salt works to recover minerals and NaCl (halite) from the brine.

1.4. Research benefit and its impact

There is no doubt that all the research completed for this study reveals huge benefits to the scientific community and specialists in hydrology. Firstly, the design methodology of the study on the impact of brine on the marine environment gives new evidence about the Libyan coastline and how it is affected by this technology, both locally and globally. Secondly, as a result of the water shortage in Libya, this gives the Libyan government a warning about the future sustainability of this technology as well as other countries that suffer from water scarcity in coastal areas. Furthermore, the recovery and recycling of salt and minerals from the brine will provide an excellent opportunity to enhance local and international infrastructures. In turn, this will give rise to increased employment and ongoing commercial and industrial growth, while reducing costs and environmental impact as well as safeguarding the continuing use of desalination technology by integrating it with renewable energy sources, such as solar power.

1.5. Research sources

Numerous books, academic articles and journals on the theory of the latest desalination plants systems and integration with the existing grid were used to gain a better understanding of the concepts and previously developed analysis and design methods. The internet is a major source of information with the most up-to-date development in desalination technologies, a range of reject brine management strategies and work related to the impact of brine disposal from desalination plants. Other sources used were primary data, collected from the field study at the sites to achieve the above mentioned aims.

1.6. Thesis outline

This thesis is structured in eight chapters. The introductory chapter (Chapter **1**) presents a background of the water situation and deficit in the Mediterranean basin and describes commercial desalination technologies and the impact of the brine disposal from coastal desalination plants. In addition, it explains methods of brine management used to reduce the volume and the impact of the brine on the environment. It also defines the aims and the objectives, the novelty of the research, benefits and impact, resources and thesis outline.

Chapter **2** presents previously published literature on desalination methods, together with the advantages and disadvantages, followed by a discussion of brine flow rates of various desalination techniques, along with the environmental and economic implications of this technology.

Chapter **3** outlines brine disposal methods used worldwide. Additionally, the benefits and drawbacks of each method are discussed. One of the challenges to coastline desalination plants, particularly in arid regions, is the dilemma of brine disposal. This chapter also presents Mediterranean legislation on brine discharge from desalination plants into the marine environment, water availability and desalination technologies in the Mediterranean region.

Chapter **4** assesses existing water resources in Libya and the impact of population growth on the available water resources in the country. It also gives the context of the current water infrastructure, the supply and demand and the ongoing challenges. Finally, this chapter is intended to expose the water deficit across Libyan regions while

also comparing the cost of water produced by the Great Man-Made River Project with a thermal desalination plant by using the Abotraba desalination plant as a case study.

Chapter **5** determines the physico-chemical effects of brine influx from thermal desalination plants on the receiving water and, pursuant to this, evaluates their impact on the marine ecosystems at the Zwuarah and West Tripoli distillation plants (ZWDP &WTRIS) on the Libyan coastline, where the marine environment is considered to be highly exposed to brine discharges.

Chapter **6** investigates the production of sodium hypochlorite (NaOCl) from an electrochemical cell fed by brine in a controlled environment on site. Within this chapter is a discussion on the effects of various critical operating parameters on this process, including, electrode materials, production of sodium hypochlorite (NaOCl), inter-electrode spacing, applied current density, energy and power consumption in addition to determining the price of utilizing the brine using the electrochemical method.

Chapter **7** supports the use of evaporation ponds as opposed to traditional salt works, to recover minerals and NaCl (halite) from brine, with particular reference to ZWPD in Libya, located on the southern Mediterranean coast. The work will also pave the way for further development of mineral salt exploitation from the brine disposed from thermal distillation plants.

The final chapter **8** summarises the overall conclusion of the contribution of this research, followed by limitations, recommendations, future work and validity of the research data collection and results. Thesis references and appendices are then presented at the end of the thesis.

1.7. Summary

The introductory chapter sets the scene of the research, its aims and objectives, the novelty of the research, benefits and its impact, resources and thesis outline. The next chapter will outline the methods of desalination technologies, together with the advantages and disadvantages followed by a discussion of brine flow rates of various desalination techniques along with the environmental and economic implications.

Chapter Two: Desalination Technologies

2.1. Introduction

The salinity of accessible fresh water on the earth is up to 10,000 ppm in contrast to seawater, which is considerably higher, ranging from 35,000–45,000 ppm in the form of total dissolved salts. The guidelines for appropriate salinity as recommended by the WHO limits it to 500 ppm, but not exceeding 1,000 ppm in special circumstances because of potential health and environmental hazards as well as economic implications (World Health Organization, 1984). Consequently, there is a need to provide water within the recommended limits of 500 ppm or less, which can only be achieved through a system of desalination and purification (Eltawil et al., 2009).

Freshwater is produced by a process of extracting excess salts and other minerals from both brackish and seawater, known as desalination. The largest sources of water reserves are oceans and seas, which are not appropriate for human consumption, so desalination is vital to the survival of the human race, particularly in more arid regions in the Middle East and North Africa where there is a ready supply of energy sources (Fath et al., 2008). The need for production of freshwater is therefore a priority for governments and industry in these and other regions with limited groundwater and surface water, due to increasing global urbanization and industrialisation (Fellows and Al-Hamzah, 2015).

Traditional methods of water supply have increased, which has made desalination a preferred option (Khawaji et al., 2008; Einav et al., 2005; Wittholz et al., 2008). Around 150 countries operated 15,988 desalination plants (including some under construction or contract) in 2011 to produce desalinated water (Henthorne et al., 2011). There was a 10% increase in the total global capacity from 2010 to 70.8 Mm^3/day in 2011. A further 632 plants were established from mid-2011 to August 2012 reaching a capacity of 74.8 Mm^3/day (Rahimi and Chua, 2017). According to the International Desalination Association, 2017 the number of desalination plants globally totalled 18,426 with a production rate above 86.8 Mm^3/day, reaching approximately 300 million inhabitants, which is testament to the supply and demand factors of desalination for both production of freshwater and energy consumption. Therefore, this chapter aims to present previously published literature on desalination methods,

together with the advantages and disadvantages followed by a discussion of brine flow rates of various desalination techniques along with the environmental and economic implications of this technology.

2.2. Desalination methods

There are several desalination processes that have been adopted, some are still in the early stages of review, but the most widely verified ones can be categorised into two types: phase change thermal processes and membrane processes as shown in (**fig 2.1**), both of which utilise specific methods. There are other methods including freezing and ion exchange, which are less popular, but all methods share conventional or alternative energy sources to produce desalinated water (Shatat and Riffat, 2012).

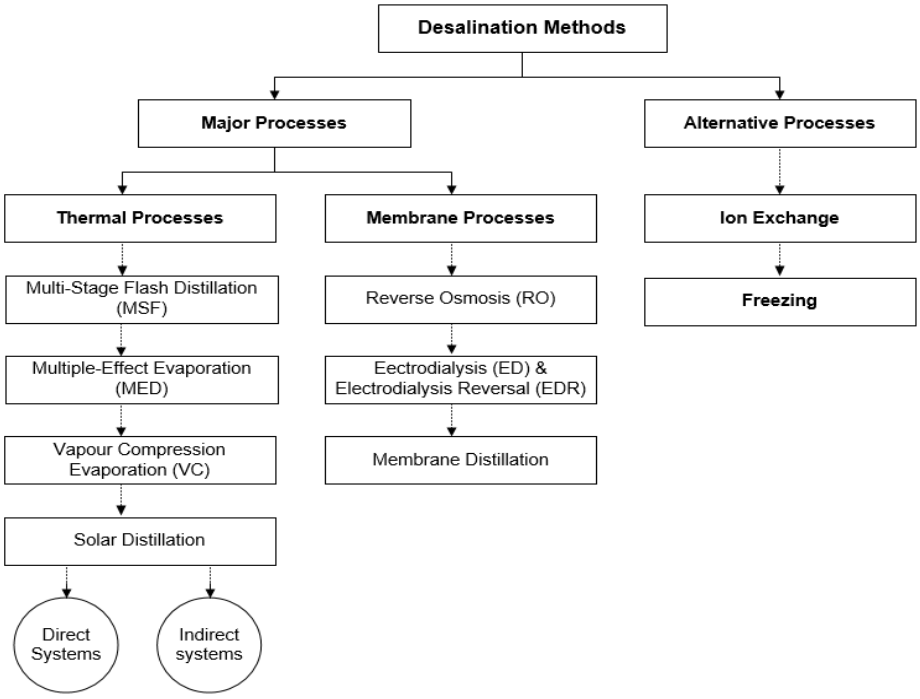


Figure 2. 1: Desalination Methods Modified from (Shatat and Riffat, 2012).

The five key elements for desalination of both brackish and seawater are divided into the following: -

I. **Intakes**: This is the location of the first stage of desalination where the source water is fed into the unit and directed to the next process.

II. **Pre-treatment**: Water is prepared by filtering and extrapolating the biological growth to ensure it is acceptable for the next stage.

III. **Desalination**: This is the main process where the salt and other minerals are extracted from the feedwater.

IV. **Post-treatment**: This is the stage where desalinated water is treated by chemical additives in order to meet the standard for human and industrial consumption.

V. **Concentrate management (Brine)**: This is the disposal of the final by-product (Brine) according to appropriate methods of desalination.

2.2.1. Thermal desalination technologies

The definition of thermal technology is the heating of saline water and subsequent collection of condensed vapour (distillate) to produce fresh water. The use of this technology is less common using brackish water because of costly overheads, although it has been used to purify seawater (Krishna, 2004) and divided into four main methods: -

2.2.1.1. Multi-stage flash distillation (MSF)

This type of distillation using flash evaporation produces water with a low salinity level (10 ppm or less) (Khawaji et al., 2008; Cooley et al., 2006). The saline feed water is passed through several tubes prior to being boiled and then condensed in the chamber or stage. Thermal energy is used to heat the brine and conveyed into a stage vessel which has a lower ambient pressure than the brine heater. At this point, a drop of pressure leads to sudden boiling (flashing) of the saline water producing vapours which condense on the tubes and subsequently form a distillate solution which can be collected, leaving only a minimal amount of steam, according to the pressure at each stage. At the next stage, the remaining water at a lower pressure continues the cycle before being discharged with salt concentrations ranging from 60,000 – 70,000 ppm TDS, at almost double the salinity of the seawater (Cooley et al., 2006). These plants can contain as many as 40 stages, but normally range between 18 and 25 stages (**fig 2.2**) (Mezher et al., 2008).

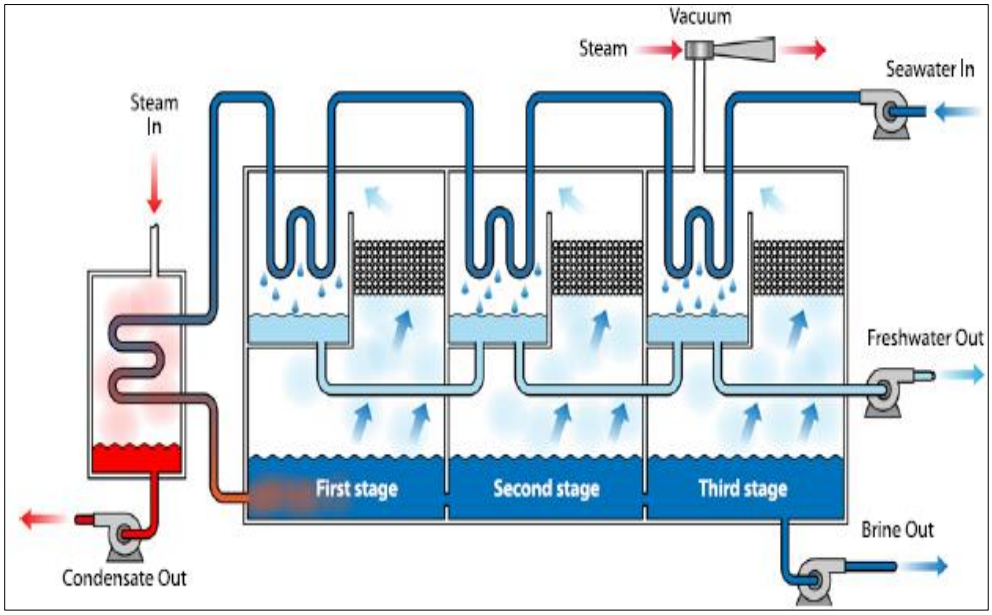


Figure 2. 2: MSF process (Al-Karaghouli and Kazmerski, 2013)

The advantages of this method are ease of construction and use of MSF plants, the effluent water (United Nations, 2001) is of a high quality at 2–10 ppm dissolved solids and does not need post treatment (Khawaji and Wie, 1994). This process does not need high purity of feed water in comparison to other methods such as Reverse Osmosis (RO). High temperatures of over 115^0C improve overall efficiency but costs can be controlled by adding more stages (Buros, 1990).

The disadvantages of this method are that although easy to construct, there are operating limits to 60% and there is a need for high energy levels (3–5 kWh/m3) electricity and 233 MJ/m3–258 MJ/m3 heat is compensated by a cogeneration system (Hamed et al., 2001). These high temperatures can result in scaling of salts such as calcium sulphate precipitate, creating thermal and mechanical issues such as clogging of tubes. Increasing the capacity of MSF plants will incur additional cost and place more demands on overall operations (Buros, 1990). Overall, this technique is more cost effective and reliable when coupled with a power station to produce industrial and potable water.

2.2.1.2. Multiple-Effect Evaporation (MED)

A similar process is the MED process (**fig 2.3**), which offers an alternative solution in that evaporation and heat transfer is used. The difference between MSF and MED is

that in the MED process, evaporation occurs from a seawater film in contact with a heat transfer surface, instead of a convective heating of seawater in tubes that results in "flashing" which is used in the MSF process to produce vapour (Wade, 2001). The MED method occurs across a line of evaporators named 'effects' and uses the reduction of ambient pressure along these effects (Khawaji et al., 2008). Water is heated by a boiler and converted to hot steam which heats the saline water in the first effect. The resultant vapour will provide the heat source for the second evaporator and subsequently heat the saline water. This process repeats itself in the third evaporator and continues thus for 8-16 stages which is common number of effects in a large plant (Saidur et al., 2011; Raluy et al., 2006).

Boiling the saline water in the fourth stage serves as a condenser for steam emitted from the previous evaporator and the same thermo-mechanical process is repeated for the whole unit on a reversing scale. The latent heat of vapour condensation is reused several times before being released outside. The temperature of the first effect should be maintained below the boiler heating system. In order to ensure an optimum heat flow between the heating vapour and the saline boiling water, temperature should be at varying degrees, i.e. the vapour pressure needs to be lower than the vapour pressure in the previous effect, but higher than the subsequent effect. Restoration of the desalinated water at an ambient pressure requires the system to be equipped with water pumps, due to stages' pressures being below the atmospheric pressure. Furthermore, the vapour space needs to be evacuated by the use of vacuum pumps until the desired pressure is reached while depleting non-condensing gases, e.g. oxygen and nitrogen which are normally dissolved in the feed saline water. Failure to remove these gases can result in preventing the water boiling and subsequently damaging the entire distillation operation. In the MED process, more than 1 ton of distilled water per ton of heating steam is produced, with an exponential increase according to the number of effects (Saidur et al., 2011). The MED systems can be combined with heat produced between stages using a range of sources, e.g. by mechanical (MVC) or thermal vapour compression (TVC) **(**Miller, 2003).

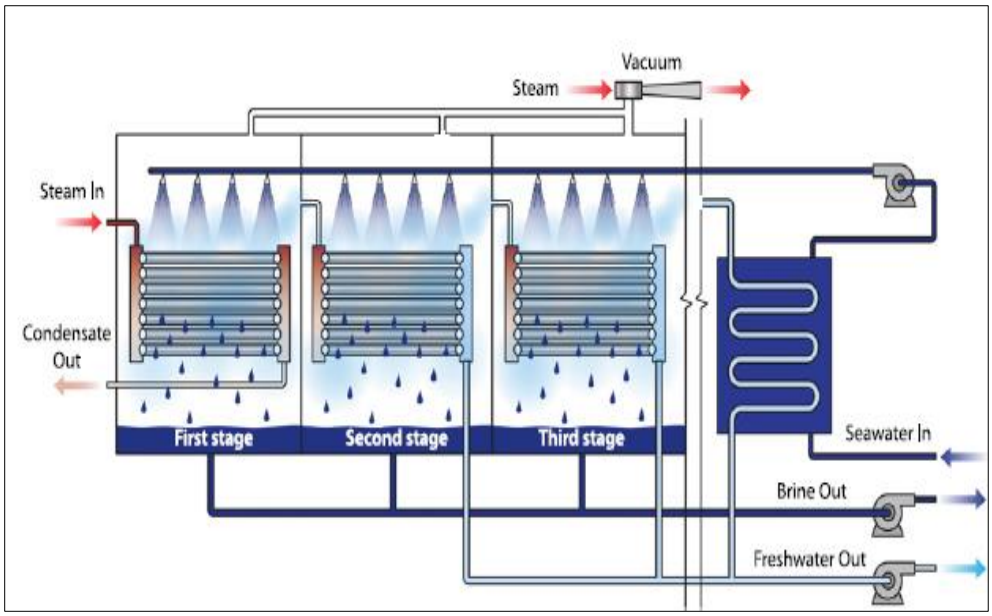


Figure 2. 3: MED process (Al-Karaghouli and Kazmerski, 2013)

The advantages of this method are that corrosion and scale build-up can be controlled by lowering the temperatures to ~ 70^0C (158^0F) (Buros, 1990). Operational and pre-treatment costs are cheaper than RO thereby reducing power demands (United Nations, 2001) in comparison to MSF. Furthermore, heat transfer and freshwater production costs are much more favourable than MSF plants (Darwish and El-Dessouky, 1996). Thus, operating costs can easily be reduced by combining MED with thermal vapour compression, thereby increasing heat transfer co-efficiency within the unit (Compain, 2012).

The disadvantages of this method are the limited operating capacity at 60%, it is incompatible with alternative inconsistent power sources. Furthermore, anti-scalants are required to prevent scale build-up in the evaporator cells (World Bank, 2012). Overall, this method is reliable when it is coupled with a power station to produce industrial and fresh water leading to a reduction in overall costs.

2.2.1.3. Vapour Compression Evaporation (VC)

This method of distillation (VC) can be used independently for small to medium scale desalination applications or in combination with other processes (such as the MED) (Buros, 1990; Mezher et al., 2008). Some of the uncondensed vapour remaining in the final stage of MED plants is compressed by mechanical vapour compression (VC) or thermal vapour compression (TVC) and used as the prime heating source for seawater

evaporation (Belessiotis et al., 2016). These processes are used in the compression cycle to run the unit. The mechanical compressor is normally powered by electricity or diesel to produce distilled water (Buros, 1990). VC distillate with one stage is equally effective as a 15-20 MED effect (Spiegler, 1977). VC units tend to range in size up to approximately 3000 m^3/day with a single stage (**fig 2.4**) while TVC systems may range in size to 20,000 m^3/day and operate multiple stages solely designed to increase efficiency and productivity of MED plants (Miller, 2003). VC units have been designed across a range of different specifications to optimise heat exchange for the purposes of evaporating seawater (Khawaji et al., 2008).

Feed saline water is preheated in a horizontal heat exchanger situated outside of the unit where distilled and brine water has collected. Non-condensing vapours such as nitrogen, oxygen and carbon dioxide are evacuated from the evaporator and condenser space using a vacuum pump or ejector at the start-up of the evaporator operation procedure (Saidur et al., 2011) in order to balance pressure and temperature of vapour and the feed water brine. A vacuum in the vessel is created by the mechanical compressor (VC) and then compressed and condensed inside a tube bundle, which is sprayed externally by seawater, producing more water after boiling and partially evaporating (Aly and El-Fiqi, 2003).

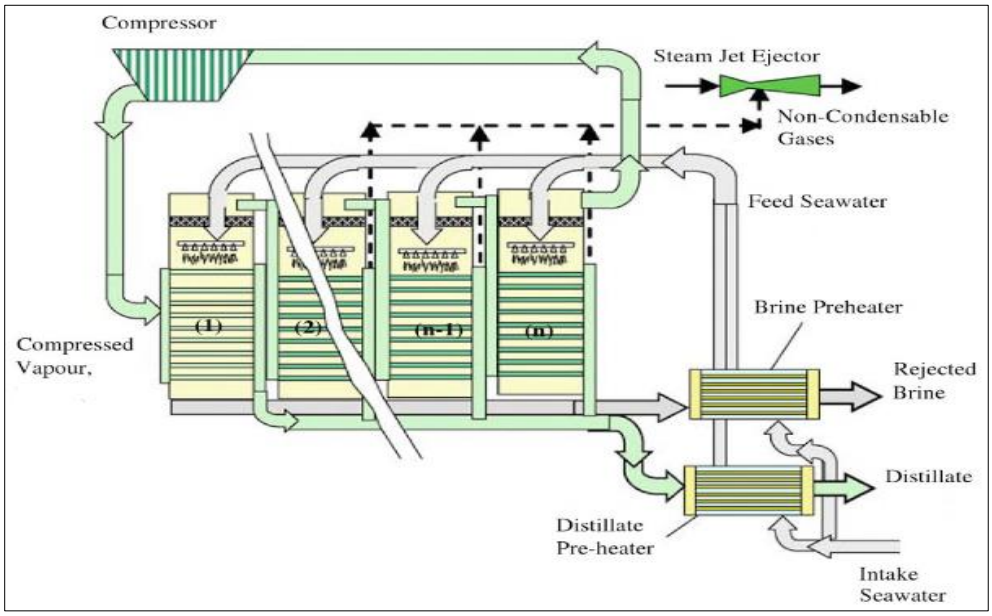


Figure 2. 4: MED process with mechanical vapour compression (Cipollina et al., 2009)

The advantages of this technique are that it works well with smaller desalination units because of basic but reliable procedures (Buros, 1990), requiring minimal power and lower temperatures, making it an easy process. Scale formation and tube corrosion is less due to operating temperatures below 70^0C (Shatat and Riffat, 2012). The only disadvantage is its low design capacity. Overall, the recent improvement in installation of the mechanical compressor (VC), particularly in thermal desalination plants, is to increase efficiency.

2.2.1.4. Solar Distillation

Solar distillation as a desalination process has long been practised, mainly for small plant operations (Schenkeveld et al., 2004), which can be divided into two categories, direct and indirect systems.

- **Direct Systems: Solar still**

The direct system is the method of heat accumulation, which powers the desalination process simultaneously in the same device naturally, known as a solar still (**fig 2.5**) (Shatat and Riffat, 2012). This comprises a blackened basin containing brackish or saline water to a specific depth, covered by a sloping glass panel to enable exchange of solar radiation and condensation (Sharon and Reddy, 2015). The panel is heated by solar energy, which heats the basin of saline water, which has been blackened to promote higher absorption of energy. Once water starts to evaporate, it produces condensation which cascades down the cooled glass panels forming droplets ready for collection as potable water (Eltawil et al., 2009).

Although the quality of water is high, the yield of water is low in the range of 2-3 l/m^2/day which is why the solar still incorporates coupling of stills with flat plate collectors, evacuated tube collectors, concentrating dish type collectors, wind turbines, booster mirrors and air conditioning units. Further enhancements to improve yield, have been the use of phase change material (PCM) and reuse of latent heat from MED units (Sharon and Reddy, 2015). Further efforts have been made to improve efficiency in the solar still, but there are common limitations of this technique for large-scale production due to the following:

- Need for extended solar collection areas

- High overheads
- Vulnerability to vicissitude of climate (Buros, 1990).

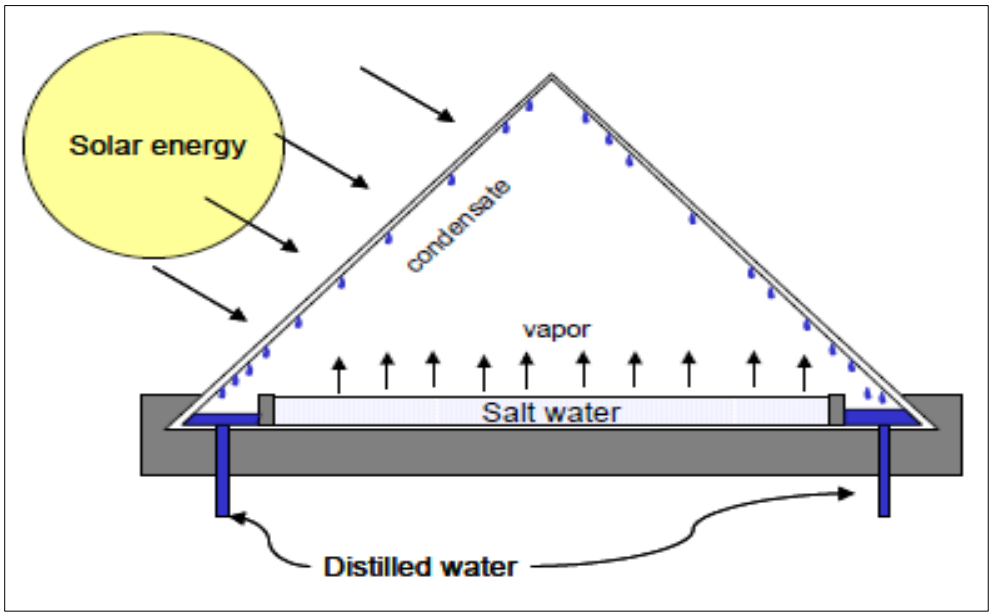


Figure 2. 5: Solar still unit (Shatat and Riffat, 2012)

- **Solar humidification and dehumidification**

The use of solar desalination humidification and dehumidification is a powerful and potential way of producing fresh water, particularly in rural and arid areas. Using an eco-friendly alternative energy source makes it a favourable one in providing fresh water (Fath and Ghazy, 2002). The process relies on water evaporation and condensation of vapour from humid air, which flows in a clockwise direction caused by an automatic exchange between the condenser and the evaporator (**fig 2.6**). The evaporator and condensation unit is placed in a thermally insulated unit. Evaporated seawater cascades slowly downwards in the evaporator where the air moves anti-clockwise against the brine becoming saturated with humidity. A residue of partially evaporated cooled brine remains in the evaporation unit with an increased saline level, while the saturated air condenses on a flat-plate heat exchanger. The basin acts as a receiver for the cascading distillate. Meanwhile, the heat of condensation passes to the cold seawater flowing upwards inside the flat-plate heat exchanger, causing the temperature of the brine to rise from 40^0C to 75^0C. Subsequently, the temperature of the brine increases to match the inlet temperature, which is between 80 and 90^0C. The brine salinity, including the condenser inlet temperature, rises in response to a partial

reflux from the evaporator outlet to the brine storage tank. This enables the distillate to be collected in a vessel while the brine is discharged to the saline water tank to recover a portion of the heat (Shatat and Riffat, 2012).

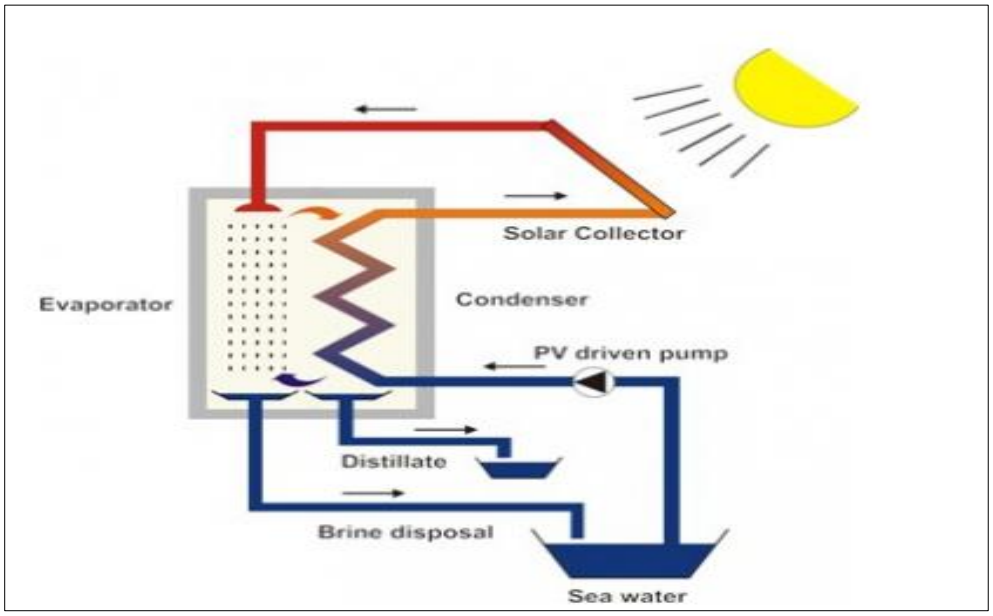


Figure 2. 6: Solar humidification and dehumidification (Shatat and Riffat, 2012)

- **Indirect systems**

This system can be divided into two sub subsystems

- A solar collector and a desalination unit. The former can be in the form of a flat plate, evacuated tube or solar concentrator which can be coupled with either of the distillation unit types previously mentioned, using evaporation and condensation principles, including MSF, VC, MED and membrane distillation (MD) for potential combinations of thermal desalination with solar energy.

- Reverse Osmosis (RO) and Electrodialysis (ED) are systems that PV devices use to generate electricity to power these types of desalination plants (Miller, 2003).

Large-scale solar desalination plants are yet to become actively operative although concern over global warming has provoked discussion for the use of solar energy for desalination plants (Clayton, 2006). Nonetheless, a recent move towards this has been

the proposal of the world's first large-scale solar-powered desalination plant with total capacity of 60,000m³ per day in Saudia Arabia (www.water-technology.net).

The advantages of this technique are that in areas that thrive on solar energy and minimal labour costs, this makes this method feasible for domestic use in less populous areas (Buros, 1990; Samee et al., 2007). In addition, thermal desalination methods can be powered by indirect systems such as those that rely on evaporation and condensation principle, i.e. MSF, VOC, MED and MD (Miller, 2003).

The disadvantages are that this technology is not feasible in urbanised populous areas as it requires considerable land area that would be in short supply and costly. Also, high costs of remedial work and ongoing maintenance together with installation makes this expensive. Selection of the best solar desalination technology is determined by several criteria such as plant capacity, location, supply of grid electricity, technical infrastructure; feed water salinity (Buros, 1990; Miller, 2003). Overall this method is suitable for remote areas where solar energy is available, such as in the Middle East and North Africa.

2.2.2. Membrane desalination technologies

Membrane desalination technology processes can be classified according to their driving force(s) as following: -

- Pressure-driven membrane methods, such as Reverse osmosis (RO), Ultrafiltration (UF), Microfiltration (MF) and Nano filtration (NF).

- Electrically powered membrane methods, e.g. Electrodialysis (ED) and Electrodialysis Reversal (ER)

- Temperature-driven membrane methods, such as Membrane Distillation (MD) and Membrane Crystallisation (MCr) (Cipollina et al., 2009**;** Krishna, 2004).

There are three major commercial desalination processes of membranes (Buros, 1990; Tsiourtis, 2001) described into the next sections: -

2.2.2.1. Reverse osmosis (RO)

Reverse Osmosis is a membrane separation technique where water is extracted from the saline solution by forcing greater pressure than the osmotic pressure of the solution (Miller, 2003). This technique is currently considered the most ideal for dealing with brackish water and seawater (Wang et al., 2011). In this process, saline water is driven by centrifugal pumps into a membrane within a closed vessel at a pressure of 15 to 25 bar for brackish water, and from 54 to 80 bar for seawater, allowing pure water to filter through the membrane while the high concentration solution (brine) is disposed of (**fig 2.7**). Two of the most effective RO membranes are designed in a spiral, wound or consist of hollow fine fibre (HFF) to deal with the feed water.

The RO applications are normally linked in a row of two or more, contained in the pressure vessel (**fig 2.8**) (Shatat and Riffat, 2012). The salt concentration of the brine effluent depends on the salinity of the feed water ranging from 20% to 70%. Some of the energy of the outgoing brine can be recovered by pressure exchangers. The main components of the RO system are a pre-treatment process, high-pressure pump, membrane assembly and post treatment process. This is the most widely used method, having a 53% global share in desalination technology production (Mezher et al., 2008).

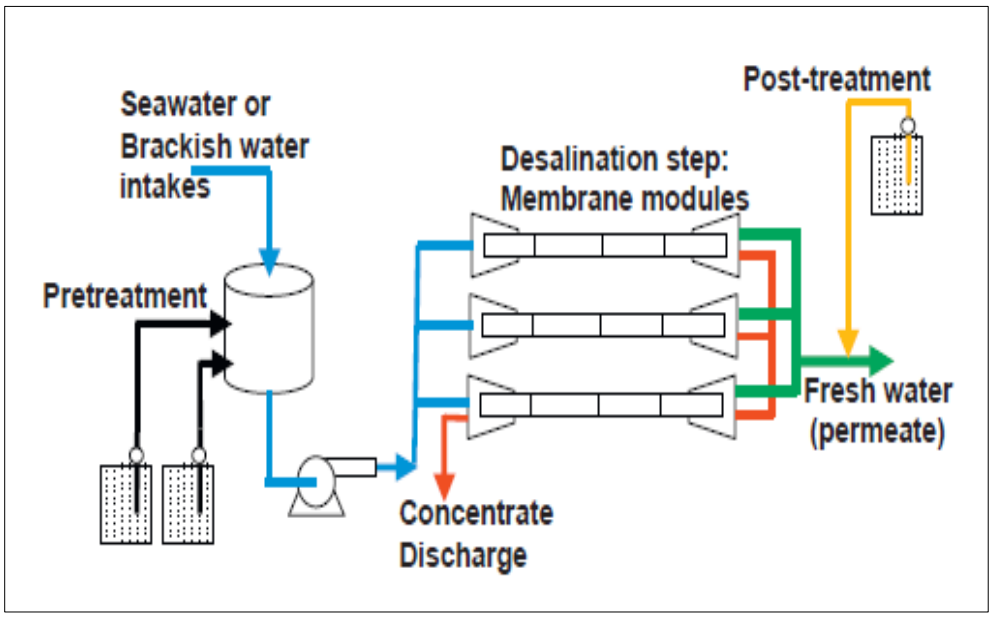


Figure 2. 7: Principle of desalination by reverse osmosis (RO) (Zander et al., 2008)

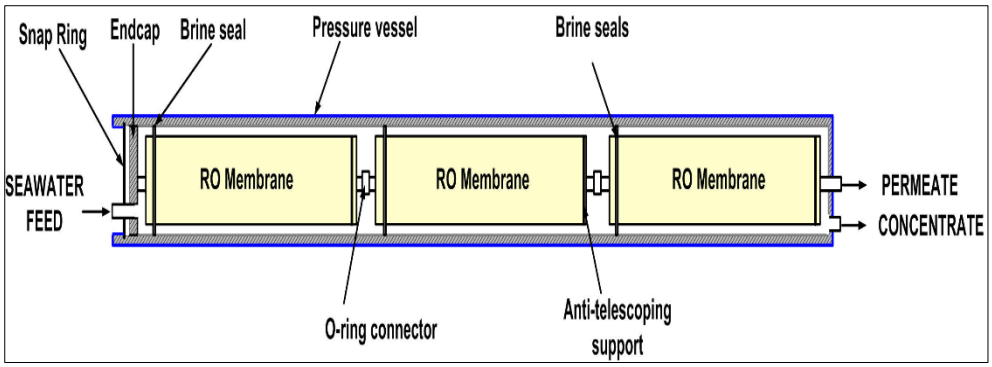


Figure 2. 8: A pressure vessel with three membranes (Lenntech, 1998)

The advantages of this technique are that the potential for corrosion is considerably reduced because of ambient temperature, in comparison with MED and MSF, and polymeric materials are favoured over metal alloys (Khawaji et al., 2008). There are two recent breakthroughs that have identified the potential to lower costs; using operational membranes that are durable and cost effective; using mechanical devices composed of turbines or pressure pumps that are connected to the concentrated steam emitted from the pressure vessel. There is a slight loss of ~1–4 bar from the level of pressure within the pump. The conversion of pressure into rotating energy makes this an economical method (Shatat and Riffat, 2012). In contrast to MSF, membrane scaling resulting from precipitated salts is considered less of a problem. Furthermore, the use of a 5-10 mm cartage micro-filter can prevent the fouling of membranes caused by large particles (United Nations, 2001).

The disadvantages of this method are that intensive pre-treatment is necessary for high salinity conditions which cause membrane fouling. Also, there is a need for highly trained staff to operate and maintain high-level design specifications. Biological fouling occurs from the entrapment of dead and live organisms and growth of micro-organism colonies causing a build-up of aluminium silicate and clays from caustic and organic materials, resulting in colloidal fouling on membrane surfaces of colloids (United Nations, 2001). A high volume of water is required in RO units, as only 5-15% is recovered from the filtered water. Typically, in SWRO plants, 40-90 gallons are disposed of for every 5 gallons of raw water (Buros, 1990). Overall, this method is widely used in EU countries because of low energy consumption due to the recent improvement in membrane technologies.

2.2.2.2. Electrodialysis (ED) and Electrodialysis Reversal (EDR)

Electrodialysis (ED) and Electrodialysis Reversal (EDR) are unique in being powered by electricity (Schenkeveld et al., 2004**)**. ED is power-driven by a direct current source together with flow channels that are divided into alternating anion and cation selective membranes for the purposes of expunging dissolved salts from the feed water. In this process, saline feed water is forced into each of the separate parallel tubes, which are linked to cation and anion voltage surges, which migrate in opposite directions. The ion concentration rises and falls in alternating channels of the equipment in response to the charge selectivity of the membranes. The distillate water is forced out under the membrane for collection, while the brine is discharged out of the unit (**fig 2.9**). Each membrane stack consists of numerous alternative channels, so as the resistance constantly changes from top to bottom, separation is conducted gradually, making it more user-friendly and cost effective (Miller, 2003). Consequently, it has become the more popular method for brackish water despite ED originally being conceived to deal with seawater (Krishna, 2004) because higher salinity and TDS tend to increase the cost. EDR was designed to deal with membrane fouling elimination (Zander et al., 2008) and involves frequent reversal of membrane polarity thereby switching brine and freshwater within the channels, breaking up and expelling any residue (Miller, 2003). Both these techniques produce very high quality distillate water that can be used in pharmaceuticals, the food industry and any other operation that uses high purity water (Valero et al., 2011; Belessiotis et al., 2016).

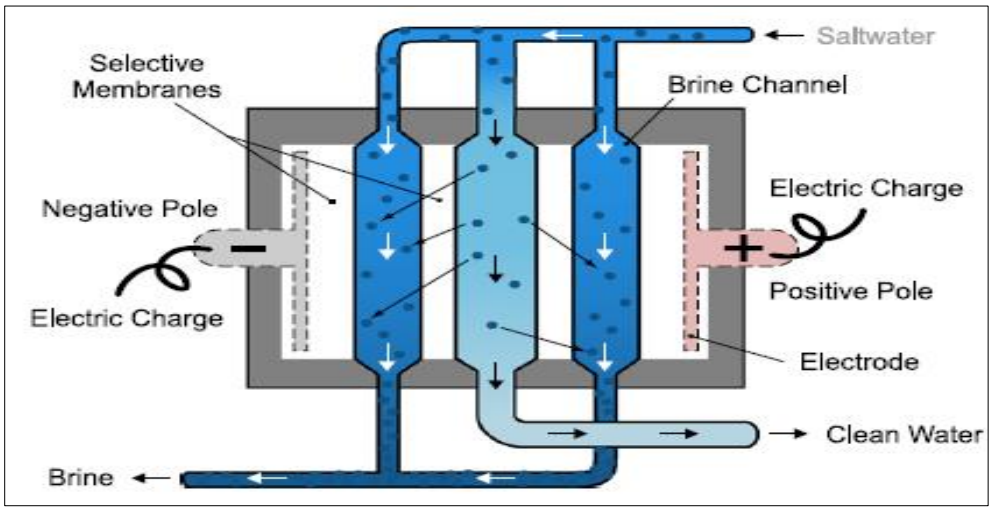


Figure 2. 9: Electrodialysis (ED) method (Al-Karaghouli and Kazmerski, 2013).

The advantages of ED method are a higher volume of fresh water being produced with reduced amount of brine (Burros 1990). Also, it can be used with brackish water with salinity of < 6 g/l of dissolved solids. It can purify feedwater with a higher concentration of suspended solids than RO with minimal pre-treatment requirement (Buros, 1990). Likewise, with EDR, there is a high recovery rate reaching 94% and there is membrane longevity (potentially 15 years in accordance with correct application). Furthermore, there is a potential for coupling with RO for improved recovery of water, reaching 98% (World Bank, 2012).

The disadvantages of ED is that it is inappropriate for water with dissolved solids of < 0.4 g/l. and use of energy is pro rota to salt removal (Shatat and Riffat, 2012). For salinity levels greater than 30 g/l, as in the case of seawater, desalination comes at a high price and is therefore not feasible (Kalogirou, 2005). The only disadvantages of using EDR is the high overhead costs compared to RO (World Bank, 2012).

2.2.2.3. Membrane Distillation (MD)

This method works on the graduation of varying temperatures with one side of the membrane being warmer and gradually cooling towards the other side. As vapour rises from the warmed liquid, it filters through the membrane towards the cooler area where a purified form of freshwater is produced from the condensation **(fig 2.10)** (Belessiotis et al., 2016)**.** Unable to pass back through the hydrophobic membrane which is permeable by vapour only, then it is trapped for collection as the output of the unit (Miller, 2003). This eliminates the transition of the liquid stage and any dissolved residue (Shatat and Riffat, 2012). Although this method was initiated for small scale operations, it has not proved to be viable, possibly due to problems of maintaining the saturation level of the membranes over prolonged periods together with fouling and membrane degradation. In addition, a large enthalpy of vaporization is required through each transition while volatile feed stream contaminants cannot always be eliminated. The possible benefits of MD is the relatively small carbon footprint it leaves compared to other methods, lower capital overheads and relatively simple power sources (Zander et al., 2008).

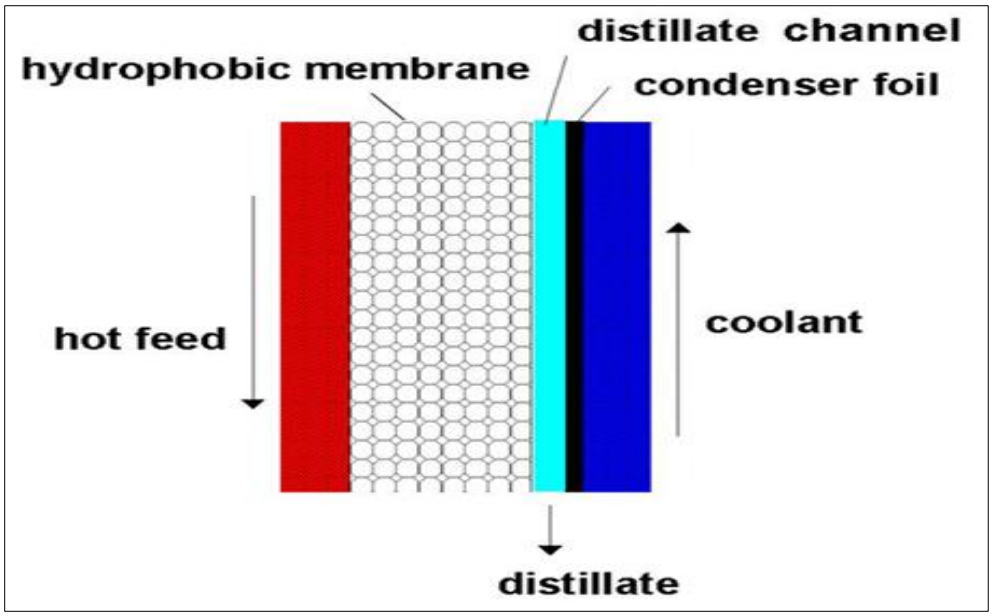


Figure 2. 10: Principle of membrane distillation (MD) (SolarSpring, 2016)

The advantages of MD are that only low temperatures are required, it is a relatively simple technology, plus the utilisation of solar energy makes this a favourable method (Buros, 1990; United Nations, 2001). In contrast to conventional desalination methods, this operates on lower pressures than membrane processes and there is less demand on vapour space. (Tomaszewska, 2000). Similar energy usage to MSF and MED plants (Buros, 1990; United Nations, 2001).

The disadvantages are a reater need for physical space, compared to other membrane processes (Buros, 1990). Also, this method is restricted because of stringent regulations on levels of organic pollutants in the feed water (United Nations, 2001).

2.2.3. Alternative processes

The other desalination methods are classified as the following:

2.2.3.1. Freezing

The method of freezing is used across a range of applications, such as fruit juice concentration, dairy products, wastewater sludge and desalination. It can also be used as a pre-treatment method for desalting of brackish and saline water which can subsequently be used in ED and RO (Mahdavi et al., 2011). This process is the method of separation of water from the solid form. As the temperature of low concentration salt water reaches freezing point, ice crystals of pure water emerge within the solution and are

mechanically separated. They are then allowed to melt back into liquid to be collected as pure water (Spiegler and Laird, 1980). The benefits of this method of freeze desalination is less energy demand and also less corrosivity of the salt solutions at lower temperatures. Therefore, cheaper materials can be used such as carbon steel fibreglass, PVC and type 304 stainless steel (Johnson et al., 1976). Freezing processes can be classified into two groups, which are outlined below:

- **Direct refrigeration**

This is the practice of using water as a refrigerant and compressing the resulting water vapour mechanically, also referred to as vacuum freezing vapour compression. A heat exchanger reduces the temperature of the salt water, which is then sprayed by a nozzle into a freezing stage. The resulting mix of brine and ice is directed into a wash column where separation takes place. Following this is the melting stage where the ice is transferred to a melting unit from which the water vapour is compressed, heated and discharged. The compressed vapour is used to heat the ice crystals to melt them and is then condensed to produce pure distillate. Finally, the pure water is collected and then pumped to a storage tank (Spiegler and Laird, 1980**)**.

- **Indirect refrigeration**

As with direct refrigeration, the temperature of seawater is reduced when pumped through a heat exchange and passed to the freezing stage, where further cooling takes place at which stage ice crystals are formed. Likewise, the ice and brine slurry is transferred to a wash column where separation takes place. The ice is conveyed to the melter where it starts to melt from heat produced from condensation of the compressed refrigerant. Some of the freshwater output is used to wash the ice crystals in the wash column, but most of it is directed through the heat exchange for the purposes of cooling the feed seawater before being discharged for collection and distribution. The remaining brine from the wash column is recycled back into the heat exchanger to cool the temperature of the feed sweater before being expelled (Spiegler and Laird, 1980**)**.

This method of freezing desalination was used in an experimental solar-powered unit built in Saudia Arabia in the late 1980s, which has since been decommissioned. Currently, this type of technology is better used in the treatment of industrial waste rather than for the production of potable water (Shatat and Riffat, 2012)

The advantages of freezing method are minimal power consumption, less likelihood of corrosion and negligible amounts of salt scaling. Also, production of very high quality drinking water, which can also be used for irrigation (Rice and Chau, 1997).

The disadavantge of this method is only elaborate techniques are needed to move and process ice and freezing water (Buros, 1990).

2.2.3.2. Ion Exchange

Ion exchange is used primarily for water softening and demineralization and its application is currently quite restricted. This method involves desalination of water, which is directed through a column of cation exchanger beads in the form of hydrogen (H^+) which eventually replace the cations in the solution that have attached themselves to the exchanger. The water is then directed through a column of anion exchange beads in the form of hydroxyl (OH^-) which is replaced by the anions that eventually combine with the hydrogen ions in the water thereby producing deionised water. Thus, this method is used for the final purification of water that has been previously treated by other desalination techniques. However, as this practice is normally coupled with other desalination techniques, is not economically feasible as a means of water purification for seawater or brackish water on its own (Zander et al., 2008).

The advantages of this method is prevalent in both industrial and commercial sectors as a method of water treatment (Tripathi, 2016), in particular when coupled with RO for the purpose of mixing RO by-product with ion exchange to augment water production (Younos and Tulou, 2005).

The disadvantage of this method is that it is not economically viable for application with brackish or seawater because of extortionate expense (Shatat and Riffat, 2012). Overall this technology can be coupled with thermal desalination plants to feed the power station in order to increase industrial water purity.

2.3. Chemical treatment procedures for desalination techniques

The description of desalination treatment processes offered (**fig 2.11**) follows the treatment procedure sequence of typical desalination techniques such as MED, MED-

TVC, MSF, and RO. Prior to any desalination technique, raw water (feedwater) needs to be chemically pre-treated to avoid scaling, foaming, corrosion, biological growth, or fouling in addition to further chemical post-treatment (Gálvez et al., 2010).

The purpose of this treatment is to ensure plant efficiency, maintain plant equipment while protecting public health and the safeguarding of the overall water distribution system (Masnoon and Glucina, 2011; Cotruvo et al., 2010). Chemical treatment procedures in desalination plants are described in the next sections:

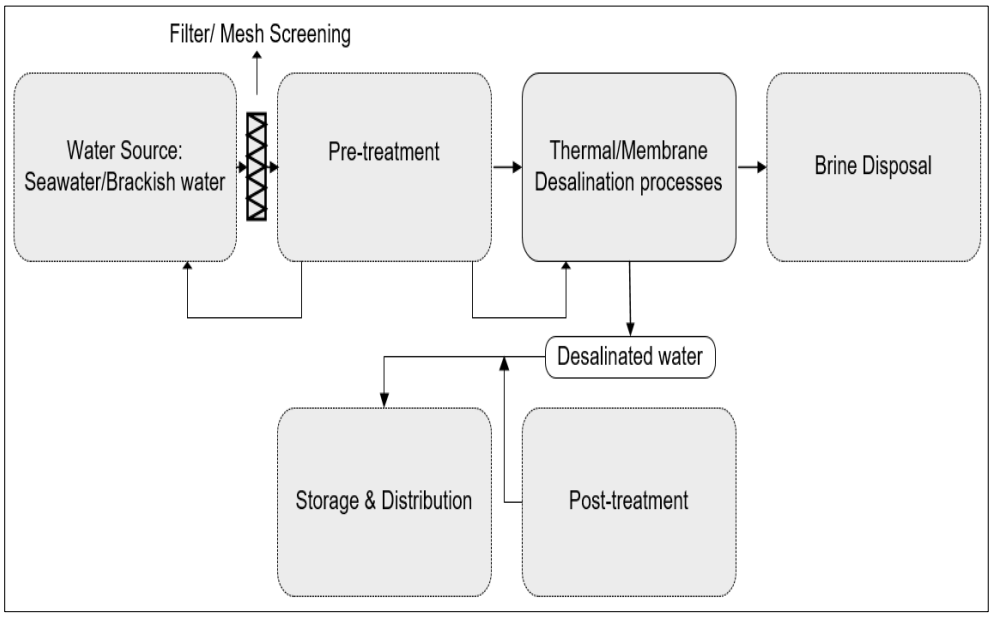


Figure 2. 11: Typical sequence of treatment procedures in desalination plants Modified from (WHO, 2007)

2.3.1. Pre-treatment of feed water to desalination plants

Prior to seawater and brackish water reaching membrane desalination systems that treat feed water from surface water sources, pre-treatment is vital to eliminate suspended and colloidal particles, organisms and natural organic matter. In the case of treatment of brackish groundwater, very little pre-treatment is necessary due to low concentrations of suspended solids and any organic matter. Nonetheless, some pre-treatment will be required to eradicate certain constituents, e.g. dissolved iron, manganese and sulphides, which can become a fouling hazard to the membranes if oxidised. Normally, feedwater is conveyed through 5 μm-size cartridge filters as a final barrier, before entering the RO units. These filters are used both with

conventional and membrane pre-treatment systems. Any remaining particles on these filters are regularly scaled off over a two-month period and disposed of in a sanitary landfill (Darwish et al., 2013). The chemicals which are most frequently applied in RO technique are presented in (**Table 2.1**).

Table 2. 1: Chemical used in pre-treatment processes for RO technique (Darwish et al., 2013; WHO, 2007)

Chemical additives name	Dosing level and location	Purpose of use and application
Oxidizing Agent or Bio-fouling (chlorine)	• Normal dosage 3.7 mg/L for 30-120 minutes repeated over 1-5 days for seawater intake. Oxidation not necessary for small RO plants that use bleach.	• To restrict emergence of marine organism at the seawater intake as well as the pre-treatment process. Also to reduce suspended material. This chemical additive is applied for SWRO large-scale plants.
Coagulant (usually ferric chloride or ferric sulphate).	• The amount of dosage of this additive is in proportion to the level of suspended material at the intake ranging between < 1 and 30 mg/L for coagulants and between 0.2 and 4 mg/L for polyelectrolytes. When ferric sulphate is injected, the dosage level for open intake of both SWRO or RO systems is f 5–15 mg/L.	• To deplete any unwanted materials from feedwater of the RO intake. This chemical additive is applied for SWRO and large-scale plants.
Flocculant Aid (usually cationic polymer).	• For expansive surface water in RO systems, and open seawater intake, common dosage ranges from 1-5 mg/l.	• To expedite suspended solids removal from the feedwater. This chemical additive is applied for SWRO and large-scale plants.
Anti-scalants (Acid addition or Sulphuric acid)	• The injection level normally varies between 40–50 mg/L depending on conditions to achieve a level of 6-7 pH in the feedwater.	• To enhance coagulation by lowering the pH to avoid further scaling. This is mainly applied in SWRO and is not always appropriate in other conditions.

In thermal processes, pre-treatment is necessary for the purposes of controlling scaling and corrosive elements of the source water. It may also be necessary to remove sand or grit-like suspended solids to protect pipes in the plants. Thermal desalination processes are favoured over SWRO because of their tolerance to seawater quality needing only basic screening at the intake, unlike the mechanical process of filtration necessary for SWRO. The main function of screening in the pre-treatment stage is to check levels of turbidity/suspended solids and that the amount of organic and inorganic foulants are within the acceptable range for the desalination equipment (Darwish et al., 2013; WHO, 2007). The chemicals, which are most frequently used in seawater pre-treatment for thermal desalination are presented in (**Table 2.2**).

Table 2. 2: Chemical used in pre-treatment processes for thermal desalination techniques (Darwish et al., 2013; WHO, 2007)

Chemical additives name	Dosing level and location	Purpose of use and application
Oxidizing Agent or Bio-fouling (chlorine)	• Regular and sporadic dosages of active chlorine at 0.5-2 mg/L depending on site conditions. 3.7 mg/L for 30–120 minutes is injected at 1-5 day intervals (≈1.0 mg/L) in expansive surface areas of seawater intake.	• To restrict emergence of marine organism at the seawater intake for all thermal desalination methods.
Anti-scalants (phosphonates, polyphosphate, polymaleic, polycarboxylic acids, or a blend of several of these)	• The point of make-up water line is where dosages of 1–8 mg/L of anti-scalants are injected while ≈100 mg/L of anti-scalants is normally injected into feedwater. To prevent growth of Mg $(OH)_2$ and $CaCO_3$ scaling, sulphuric acid (H_2SO_4) is injected to reduce the pH although it is not often used.	• To control the growth of (Mg(OH)2 and (CaCO3) deposits for all thermal desalination units
Antifoams (Poly Othelyne Ethylene Oxide or similar Surfactant)	• Make-up water is dosed with 0.1 mg/L antifoam.	• To prevent foaming within the evaporator cells, applied sporadically in all thermal processes, but mostly in MSF.
Sodium bisulphite	• Make-up water is injected with ≈0.5 mg/L of sodium bisulphite.	• To control corrosion by removing amounts of residual oxygen or chlorine in saline water circulation,

used in MSF plants as well as MED.

2.3.2. Post treatment of the produced desalinated water

The constitution of desalinated water that has been directly produced from either thermal or membrane processes, tends to be low in mineral content, alkalinity, and pH. Therefore, post-treatment is important to reduce corrosion which can damage pipeline materials, metals and concrete and could potentially change metal levels in potable water, thus limiting the longevity of the overall water-system infrastructure. The post-treatment of product water involves the use of certain additives, which are described below: -

- Calcium hydroxide (slaked lime) to increase the hardness and alkalinity.
- Sodium hydroxide (caustic soda) to adjust the pH.
- Carbon dioxide is commonly used to normalise the pH.
- Disinfection (Zander etal.,2008;Cotruvo etal., 2010)

2.4. Brine discharge flow rates for desalination methods and its impact on marine environment

The volume of brine discharged from desalination is greater than the volume of freshwater. The effluent is normally mixed with cooling water prior to being discharged and has high salinity combined with chemical contaminants which pose the greatest threat to the marine environment. In general, seawater or brackish water when passed via desalination process produces about 40% of fresh water and 60% of brine (**fig 2.12**). The composition of the chemical additives used during desalination process is outlined below:

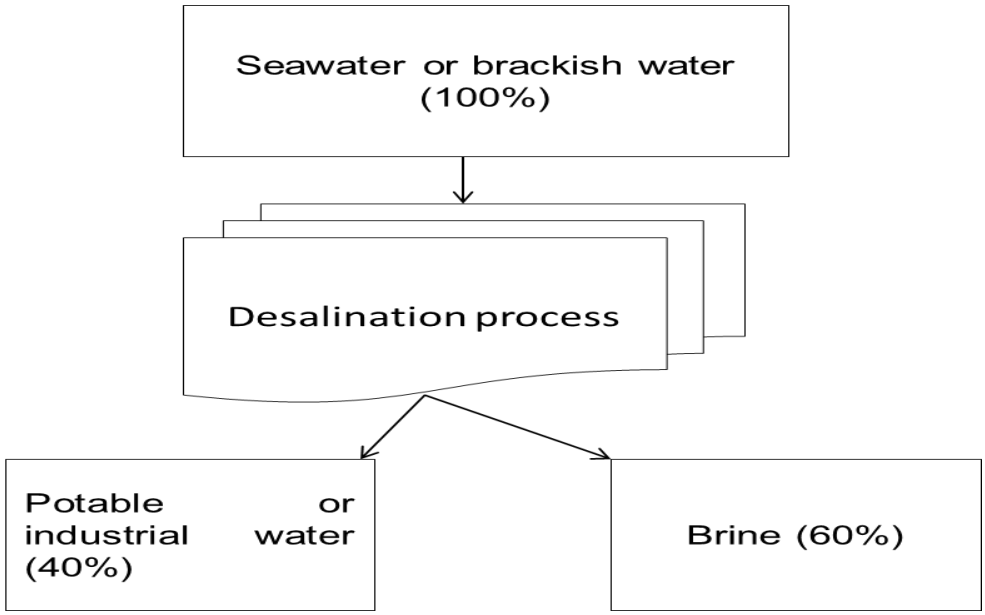


Figure 2. 12: Mass balance in desalination process Modified from (Trieb, 2007)

2.4.1. Bio-fouling agents

Chlorination, namely Chlorine (Cl_2) and sodium hypochlorite (NaOCl) is normally used to prevent bio-fouling at seawater intake with typical doses of 0.5-1.5 mg/l (Al-Dousari et al., 2012; Darwish et al., 2013). In thermal desalination plants, levels of residual chlorine concentrations of 200 and 500 μg/l are indicated for the effluent, equalling 10-25% of the dosing concentration. This dosing level guarantees protection against bio-fouling from intake to discharge but it also results in residual chlorine reaching surface waters which constitutes a hazard to marine life. In RO plants, membranes are protected by de-chlorination using polyamide membranes although there is still the possibility of residual chlorine levels existing in the effluent which exacerbates the issue of toxic halogenated organic compounds (Lattemann and Höpner, 2008). In addition to this, sodium bisulphite ($NaHSO_3$), widely used for de-chlorination, can have adverse reactions with harmless products while depleting oxygen levels to a critical level if overdosed. In addition, there are serious repercussions of the chlorine and its by-products due to carcinogenic and environmentally damaging properties, which raises concern for public health.

Seawater consists of approximately 6.5 mg/L of bromide (Br^-) which when oxidated during the chlorination process, forms bromine (Br_2) producing organobromine compounds. Consequently, trihalomethanes (THM) in chlorinated seawater mainly

consist of bromoform ($CHBr_3$) and dibromo-chloro-methane ($CHBr_2Cl$). The end product in the oxidation of organic substances is bromoform which develops gradually, so these two compounds have become subjects of identification and research. The resulting residual oxidant in the coolant water normally ranges from 0.1–0.2 mg/l. Despite the low level of organo-chlorinated by-products present in the chlorine, they tend to be more prevalent than residual chlorine, thereby constituting further hazards to the marine environment (Darwish et al., 2013).

2.4.2. Coagulants

Ferric chloride ($FeCl_3$) or ferric sulphate ($FeSO_4$) is used as a primary coagulant or flocculant in the pre-treatment system of existing SWRO plants to deal with media filtration of suspended material. Following sporadic backwashing of the media filters, the suspended debris and coagulants are expelled into the ocean without treatment. The toxicity of the chemicals is minor although there may be coloration of the reject stream when ferric salts are used ("red brines"). This can cause increased turbidity while limiting light penetration, which could have a harmful effect on marine organisms in the location of discharge (Lattemann and Höpner, 2008).

2.4.3. Antifoams

These are organic (acylated polyglycols, fatty acids and fatty acid eaters) or silicon-based compounds (composition undisclosed by manufacturers but certified as being non-toxic), which are added to the feedwater. It is currently unknown what damage they can cause to the marine environment, or their level of toxicity (Darwish et al., 2013), but it could be widespread due to low rate of biodegradation (Lattemann and Höpner, 2008).

2.4.4. Oxygen scavengers

There are two methods normally used to extract oxygen from the feedwater of the boiler in thermal desalination plans. The first method is known as mechanical de-aearation, which is normally used in the feedwater of the boiler, by means of a mechanical tower, which causes reduction of the oxygen level in the feedwater, prior to entrance to the boiler. The second is the addition of chemical oxygen scavengers such as Sodium sulphite (Na_2SO_3) or Hydrazine (N_2H_4) for the principal purpose of corrosion inhibition. In order to increase the pH level and to reduce the risk of acid

corrosion, hydrazine, is widely used in the feedwater of the boiler at high temperatures and pressure, but it has been classified as being highly hazardous, thereby posing serious repercussions for the environment (Plumley, 2005; Darwish et al., 2013). The other oxygen scavenger is sodium bisulphite which is commonly used to prevent membrane damage in RO plants by removing residual chlorine from RO feedwater but in cases of overdosing, oxygen levels be may depleted (Abuzinada et al., 2008). Overall, a low level of oxygen in the seawater may cause harm or damage to marine life.

2.4.5. Acids and alkalis

The Sulphuric acid (H_2SO_4) is injected to the feedwater to make calcium carbonate ($CaCO_3$) and magnesium hydroxide (MgOH) more soluble calcium and magnesium sulphate salts and in order to shift the pH above 9.0, sodium hydroxide (NaOH) is added to seawater feed. The ionic composition of the brine discharged is barely affected by sulphuric acid or sodium hydroxide, therefore not constituting any kind of threat to the environment (Darwish et al., 2013).

2.4.6. Heavy metal (corrosion products)

Heat exchanger materials are normally made of copper-nickel alloys which presents problems to thermal plant reject streams because of potential brine contamination from the corrosive copper. A combination of various metals such as iron, nickel, chromium and molybdenum are present in the brine discharged from RO plants, but the use of non-metal equipment and stainless steels ensures that contamination is kept to a minimum. However, a higher level of heavy metals can be produced as a result of antiscaling and use of acids. This increased concentration of copper in the sediment poses cause for concern at the discharge point because it is understood that any toxic spills can occur at molecular/cellular levels and have organismic effects. Copper, nickel, chromium and other metals that could be released can have harmful effects on marine flora and fauna (Lattemann and Höpner, 2008; Hoepner, 1999).

2.4.7. Scale inhibitors

The prevention of scale formation in the feedwater in both thermal and RO plants is achieved by the use of antiscalants (Lattemann and Höpner, 2008). One of these is

known as polyphosphate, which hydrolyzes to orthophosphate at a temperature of approximately 90°C. Primary production is enhanced by the nutrient of orthophosphate resulting in the growth of algal blooms at the discharge point so the BELGARD EV2000, a polymer of maleic acid is used as a replacement to the polyphosphate. It is not considered toxic in potable water and is widely recognised although its reputed eco-toxicity is still undecided; even though the BELGARD EV is considered user-friendly (Dweiri and Badran, 2002), research is still inconclusive as to the degradation of these anti-scalants and their impact on the marine environment (Darwish et al., 2013).

2.4.8. Salinity and temperature

The discharged brine from RO plants normally has a salinity of 60-70 psu but this level is influenced by the salinity concentrate of the intake feedwater. In thermal desalination plants, the brine blowdown could have a similar level of salinity of 70 psu but is less concentrated when it is mixed with three times the volume of cooling water (seawater) which dilutes it to a level of around 50 psu prior to discharge. In thermal desalination plants, the temperature of the discharge ranges 5-15 ^{0}C above ambient temperatures whereas temperatures of RO discharge tend to be similar to ambient seawater temperature (Abuzinada et al., 2008). The outcome of these high levels of salinity and temperatures can have a devastating effect on marine life. (Lattemann and Höpner, 2008).

2.4.9. Cleaning chemicals

The type of fouling dictates the method of cleaning, in RO plants the removal of silt deposits and biofilms from membranes is achieved by alkaline solutions (pH 11-12) while metal oxides or scales are dissolved by the application of acidic solutions (pH 2-3). Other chemicals may be added to these chemical solutions to improve their efficacy such as detergents (e.g. dodecyl benzene sulphonate, dodecyl sulphate) or oxidants (e.g. sodium hypochlorite, sodium perborate). On completion of cleaning and prior to storage, it is normal practice to disinfect membranes by the application of oxidizing biocides (e.g. hydrogen peroxide and chlorine) or non-oxidizing biocides (e.g. isothiazole, glutaraldehyde or formaldehyde). Heated acidic seawater is used to cleanse the distillation plant in removing alkaline scales from heat exchanges surfaces

where corrosion inhibitors may have built-up (e.g. benzotriazole derivates). When these chemical solutions are expunged after cleaning in a raw form, there is potential threat to marine life (Lattemann and Höpner, 2008).

2.5. Air emission

Due to temperatures up to 120°C required in distillation plants such as MSF stations, there is heavy demand on thermal and/or electrical energy from desalination plants: for every cubic metre of fresh water produced, 12 kW h of thermal energy and 3.5 Kw h of electrical energy are required. In MED plants, the temperature is considerably less at (<70°C) requiring only 6 kW h of thermal and 1.5 kW h of electrical energy per cubic metre. For the RO plants, only 4-7 kW h/m^3 is needed according to the capacity of the plant and power recovery installations (Lattemann and Höpner, 2008). Thus, it can be seen that all these methods require substantial levels of energy resulting in release of toxic gases e.g. CO_2, CO, NO, NO_2, and SO_2. The level of the former is approximately 25kg/m^3 of produced water. In addition, the use of traditional power sources such as fossil fuels to generate the energy, also has serious implications for the air quality, therefore alternative sustainable energy sources should be considered in the future to overcome the effect of these noxious gases (Darwish et al., 2013; Al-Karaghouli and Kazmerski, 2013).

2.6. Economic cost of desalination technologies

Although the cost of desalination processing has dropped due to developments in the technology, the actual overheads incurred in sourcing and treating water from conventional reserves have risen due to required compliance with health and safety regulations regarding water quality control. In fact, the cost of desalinated water remains more than double the cost of water from traditional water sources. These costs vary regionally and globally. For large-scale freshwater production from the seas, the options to use either thermal processes (MSF, MED, MED-TVC) or membrane (RO) will influence the ultimate expense dependent on plant capacity and output, together with environmental factors (Khawaji at el., 2008). These include seawater properties, quality of produced water, energy source and utilisation, plant size and efficiency, levels of concentration of discharge, staffing, area required and overall maintenance. The direct costs are factored into the economic calculations, e.g.

capital, energy, manpower, chemical additives, consumables and raw materials (Darwish, 1989; Wade, 1993; A1-Sahlawi, 1999).

Desalination economics is determined by an assessment of life cycle costs using an equal uniform annual cost method where capital costs are at a fixed annual rate in contrast to a variable rate for operation and maintenance overheads. An average figure for water production based on both capital and operation and maintenance costs, is determined in \$/ m^3 by the division of total costs by total water volume produced (Khawaji et al., 2008). In the case of thermal desalination plants with large-scale operations of MSF, where water production ranges between 23,000 and 528,000 m^3/day, the estimated costs are from 0.52 to 1.75\$/m^3. In contrast to MED plants producing over 90,000 m^3/day, the estimated costs range between 0.52 and 1.01\$/m^3. For medium sized MED plants, costs are lower, ranging between 0.95 and 1.95\$/m^3 for production of 12,000 to 55,000 m^3/day. The cost of Vapour Compression in small-scale operations with capacity of approximately 1000 m^3/day ranges between 2.0 and 2.60 \$/m^3. In contrast, the costs of RO water production have fallen due to advances in membrane technology. For large-scale SWRO plants utilizing between 100,000 and 320,000 m^3/day, the estimated cost of water production ranged between 0.45 and 0.66 \$/m^3. For medium-sized SWRO plants processing between 15,000 and 60,000 m^3/day, the water production cost was estimated from 0.48-1.62 \$/m^3. In the smaller SWRO plants with a capacity ranging from 1000 to 4800 m^3/day, prices were reported between 0.7 and 1.72 \$/m^3. While for brackish water, the most cost effective methods of water desalination are RO and ED, the former can be used with TDS greater than 500 ppm, whereas ED is more economically viable for lower concentration of TDS. The cost of water production for BWRO with a capacity of 40,000 to 46,000 m^3/day is estimated at 0.26- 0.54\$/m^3, in contrast to smaller ED plants estimated at 0.6 to1.05\$/m^3, according to salinity concentration of the feedwater (Karagiannis and Soldatos, 2008; Mezher et al., 2008).

A favourable alternative is the use of solar distillation for the purposes of water desalination because it is a simple method with low overheads without any need for fossil fuel to heat the water. Nonetheless, low productivity of the still means reduced economy of scale making it a less viable option. With production rates from 4 to 6 l/m^2, the estimated cost ranges between 1.3 and 6.5\$/m^3 (Al-Karaghouli and

Kazmerski, 2013). Other methods using freezing and melting processes have been reviewed by Youssef et al., 2014 and Johnson et al., 1976 confirming costs between (0.34 to 2.45\$/m^3) using a capacity from 1 to 3.8m^3.

In terms of capacity and water volume, it has been reported by Voutchkov (2010) that costs are influenced by economies of scale. This was also conceded by Colley and Ajami (2012) who verified that the difference in desalination capacity between 50 MGD and 10 MGD can influence an upward change in final costs estimated between 2.17\$/m^3 and 7.96\$/m^3. A study of varying costs of desalination methods including SWRO, BWRO, MSF and MED has been completed by Wittholz et al., 2008 dealing with a range of capacities are presented in (Table 2.3).

Table 2. 3: Cost of desalinated water for commercial desalination technologies with different capacity (Wittholz et al., 2008)

Methods	Capacity (m^3/day)	Capital cost (\$× 10^6)	Cost of water (\$/m^3)
SWRO	10,000	20.1	0.95
	50,000	74	0.70
	275,000	293	0.50
	500,000	476.7	0.45
BWRO	10,000	8.1	0.38
	50,000	26.5	0.25
	275,000	93.5	0.16
	500,000	145.4	0.14
MSF	10,000	48	1.97
	50,000	149.5	1.23
	275,000	498.1	0.74
	500,000	759.6	0.62
MED	10,000	28.5	1.17
	50,000	108.4	0.89
	275,000	446.7	0.67
	500,000	734	0.60

2.7. Summary

As ready supply of water become diminishes in many parts of the globe, the demand for desalination is constantly rising as population, industry and commerce burgeon. This chapter has reviewed different methods of water desalination that have emerged over the past years while also reporting on operating costs and evaluating the various methods. Membrane desalination processes are seen to be more sophisticated in terms of recent technological development, energy recovery and pre-treatment making it a preferred option over thermal processes. SWRO is shown to be more cost competitive

for seawater, compared to thermal distillation processes such as MSF and MED because of streamlined operations requiring less use of chemicals, higher operating efficiency and overall control of scaling and anti-fouling. Meanwhile, the use of membrane technology for brackish water incurs less cost than seawater membrane desalination due to low salinity. On the other hand, for large-scale plants such as MED and SWRO, costs are lower than MSF because of economy of scale and efficiency under most local conditions.

Clearly, there is a need to consider environmentally friendly alternatives to avoid further depletion of water sources and climate change. The concept of combining desalination plants with eco-friendly renewable power sources has become a pressing and controversial topic due to ever increasing fossil fuel costs and the deleterious effects of combustion of traditional fuels on the environment. This dilemma is influenced by factors including the plant size, type of feed water and geographical location.

As the search for a solution to deal with water scarcity continues in assessing the best method of desalination, there is concern about the brine discarded from desalination plants, particularly huge capacity stations, which are constructed on the coastline. This effluent contains chemical additives, which are normally added in the pre-treatment process, so compounded with high salinity and temperature, this could have several knock-on effects on the surrounding environment. The next chapter will present the methods of brine disposal from desalination plants.

Chapter Three: Brine Disposal Management Options for Desalination Technologies

3.1. Introduction

The management of brine disposal has long been a topic of concern due to certain factors such as the increasing number and size of desalination plants, particularly in arid and semi-arid areas, that impacts on disposal options, the regulations governing disposal and environmental implications (Mickley, 2006). Several techniques for disposal and volume reduction of the brine waste have been tested and pioneered without which the production of brine and treatment of produced concentrate could not be achieved. This is a key component of the operation of desalination plants and its handling of concentrate, so is critical to effective operation. The location of desalination plants dictates the type of process used, whether distillation or membrane technology and the best method of brine disposal (Masnoon and Glucina, 2011; Ahmed et al., 2009; Jirka, 2008).

The option of brine disposal in inland and coastal areas varies according to discharge. The simplest and cheapest method is into the ocean, hence its practice by coastal desalination plants, the rapid mixing dilution makes it the safest disposal option (Ahmed et al., 2001). For inland areas, this is not a feasible option, as the disposal costs of inland desalination plants such as RO plants are higher than those of plants disposing reject brine in nearby seas or lakes. Consequently, alternative methods have to be adopted that do not pose economic or environmental threats (Svensson, 2005). The waste cannot be used for agricultural or commercial purposes, so this presents challenges of exploiting brackish water sources for any other purpose (Glueckstern and Priel, 1996). In this case, the waste cannot be recycled or disposed of safely, which has an ongoing impact on the environment (Sethi et al., 2007). There are certain options for disposal of reject brine from inland areas such as discharge to surface water or wastewater treatment plants, deep well injection, land application, evaporation ponds and zero liquid discharge in addition to some brine volume minimization techniques currently being explored and used (Sethi et al., 2006; Masnoon and Glucina, 2011).

Awareness of the need for environmental regulations varies hugely around the world. In the Middle East, where about two thirds of desalination plants and oilfields are located, monitoring is less regulated, with inadequate brine disposal systems (Einav et al., 2002). The same applies to other countries, for example, Libya where, despite the current environmental legislation law no 14/1989 being in place, there is little regard for maintaining the required standards of safe disposal (Nait, 2015). In other countries nonetheless, the regulations are adhered to (Ahmad and Baddour, 2014).

At the outset of establishing desalination plants, brine disposal processes dominate the decision-making in terms of their economic feasibility (Abdul and Weshahi, 2009). Clearly, the cost factor determines the proposed method, ranging from 5% - 33% of the total cost of desalination. It is influenced by reject brine characteristics, the required level of treatment prior to disposal, the means of disposal, volume of brine and the receiving environment (Ahmed et al., 2001).

Overall, this chapter, therefore, aims to outline what kind of brine disposal methods are being used worldwide. Additionally, the advantages and disadvantages of each method will be discussed. As one of the challenges to coastline desalination plants, particularly in arid regions, is the dilemma of the brine disposal, this chapter also presents Mediterranean legislation of brine discharge from desalination plants into the marine environment and the water availability and desalination technologies in Mediterranean region.

3.2. Brine Discharge Management Methods

3.2.1. Surface Water Disposal

There are several methods of surface water disposal into water bodies such as ponds, streams, lakes and coastal waters such as estuaries, bays and oceans (Younos, 2005). These involve the installation of various controls, such as outfall diffusion devices and the dilution of brine by mixing it with less concentrated streams, in order to reduce the impact on the environment (Sarté et al., 2006). There is a more in-depth explanation in the next sections.

3.2.1.1. Direct discharge

This technique is the most favoured with over 90% of desalination plants using it for discharge directly to the sea (WHO, 2007). However, this intensifies the salinity along the coastline which compromises the quality of coastal and groundwater aquifers due to salinity intrusion (Purnalna et al., 2003). Brine can be mixed through tidal movements or it can be discharged outside the tidal zones using outfall diffusers in the mixing zone to enhance the process (WHO, 2007). This method may be a feasible option for smaller desalination plants but would not be environmentally viable for discharge into freshwater bodies such as rivers and lakes (Masnoon and Glucina, 2011).

3.2.1.2. Discharge to outlet of the power plant

The technique of dilution of concentrated brines using hot water discharged from the power station is commonly practised. This is achieved by a hybrid installation, which is a desalination plant co-located to a power station. The brine is mixed with power plant cooling water within the outfall line from the power station, using a discharge line outfall, before going to the sea (Einav et al., 2002). This option is environmentally friendly because of reduced salinity concentration (Abdul-Wahab and Al-Weshahi, 2009).

3.2.1.3. Discharge via wastewater treatment plant

This technique is used where a desalination plant is situated close to a wastewater treatment plant. A positive outcome of combining the brine discharge with wastewater is dual dilation, which reduces the density of concentrate (WHO, 2007). However, this can result in the production of calcium carbonate on filters which impacts on the efficiency of wastewater treatment plants (Squire, 2000). The main considerations therefore are availability and cost of wastewater outfall capacity and the potential for whole effluent toxicity resulting from an ion imbalance of the blended discharge (Mickley, 2006).

3.2.1.4. Discharge to sewage system

This option involves discharge of brine into a nearby sewage system from small brackish water and seawater desalination plants into large-capacity wastewater treatment facilities (WHO, 2007). The result of this mixed blend would not be

appropriate for use in irrigation, so consideration needs to be given to the capacity of the sewage system (Ahmed et al., 2000).

3.2.2. Deep well injection

The disposal of industrial, commercial and liquid hazardous waste is currently done by deep well injection (Saripallia et al., 2000). This method has been considered for land brine disposal, which involves injection of brine from desalination plants into compatible deep underground aquifers that do not use potable water. The design ensures that potable water sources are kept separate from the aquifers to avoid contamination (Glater and Cohen, 2003; Masnoon and Glucina, 2011). This is an expensive process and is widely used in Florida, which has beneficial hydrogeological conditions (Reimold et al., 1996; Mickley, 2001). According to a study by Skehan and Kwiatkowski (2000) who looked at design criteria, deep well injection is the optimum method compared with other systems in practice for inland desalination plants. Mickley (2009) has also affirmed these benefits, but stresses the need for maintenance of a long-term operation to effectively dispose of large amounts of process fluid.

3.2.3. Land application/Spray irrigation

Land application and spray irrigation is an alternative method of brine disposal, used for landscape and irrigation purposes (Masnoon and Glucina, 2011). Methods used are spray irrigation, rapid infiltration, percolation ponds and overflow application (Younos, 2005). Areas that benefit from spray irrigation need to be salt tolerant, such as grasses and vegetation in lawns, parks, golf courses or cropland (WHO, 2007). A lesser concentrated brine of reduced volume is used in land application in order to meet groundwater criteria. The target vegetation must be salt tolerant and comply with ground water quality standards. Other factors to be considered are availability and cost of land, percolation rates and irrigation needs (Mickley, 2009), and during heavy rainy seasons, there needs to be an alternative disposal method (Squire, 2000). Currently according to a study, Florida is the only state that uses land application for this disposal method (Younos, 2005). A study in the UAE revealed that discharge of brine resulted in groundwater contamination and a hardness of groundwater due to inappropriate design standards (Mohamed et al., 2005).

3.2.4. Landfill disposal

An alternative option of brine disposal methods is conversion of brine from liquid to a solid mass, to be disposed in landfill. This is used as a final disposal mechanism of brine, e.g. brine concentrators. There is a risk of leakage from landfills into nearby groundwater, so site selection needs careful consideration (Masnoon and Glucina, 2011). Normally, landfill must consist of a minimum of 50% of solid masses, so the liquid remainder would need to be contained in drums, involving costly transportation and permit fees, which vary across landfill facilities (Kepke et al., 2008).

3.2.5. Zero liquid discharge

Zero liquid discharge methods are commonly practised in industrial zones that do not permit discharge (Davis, 2006). This involves a sequence of brine evaporation, crystallisation or spray drying to produce a resultant solid mass consisting of solidified salts and mineral slurries that are later taken to landfill, or used for commercial purposes (Masnoon and Glucina, 2011).

3.2.5.1. Evaporation ponds

Evaporation ponds are commonly used to dispose of brine from inland RO desalination plants in desert-type terrain such as in North Africa and the Middle East (El-Naas, 2011). It is done by a gradual evaporation of water in large ponds through solar energy, leaving wet salt residues (Leong et al., 2014). This is a less common method with only 6% being used in the USA in 1993, which later fell to 2% after 1993 (Abdul-Wahab and Al-Weshahi, 2009). This may be attributed to the large amount of land needed and the fact that very few desalination plants are based inland. Furthermore, there are potential environmental issues such as strict design requirements and pond leakage causing contamination of groundwater in the area. The most recent models are lined with polyvinyl chloride, high-density polyethylene, butyl rubber and hypalon to prevent leakage and seepage of contaminants into the nearby groundwater (Morillo et al., 2014). The effectiveness of evaporation ponds is dependent on the evaporation rate, which is influenced by the climate, including humidity and temperature so wind-aided intensified evaporation options have been tested to improve the evaporation rates. However, this is still unpredictable and is

only 50% effective in dry conditions (Gilron et al., 2003). Another contributory technique to speed up the process, is having a greater water surface for optimised exposure, using spraying or misting movements of water, in addition to use of saturated textiles to increase exposure. However, the downside to these methods is the dispersal of mist and dry salt particles although they would reduce the amount of land required and the capital costs (Mickley, 2009). Consequently, the use of evaporation ponds is more cost effective for smaller brine flows and coupled with high recovery desalination process (Masnoon and Glucina, 2011). Further costs are alleviated by the introduction of particular synergies that provide income in combination with these ponds, as described below: -

A. Aquaculture

A new cutting-edge industry is aquaculture, which can be used to culture fish. Several species are reported to thrive in high salinity in Australia, namely Barramundi (*lates calcarifer*), Red Snapper (*Pagrus auratus),* Black Bream (Acanthopagrux butcheri), Milk fish (Chanos chanos),), Mullet (Mugil cephulux), Tilapia (Oreochromis mossambicus) and brine shrimp (*Artemia salina*). There is a mutual relationship between fish and shrimp production where each can benefit. In addition, the brine shrimp act as 'cleaner' of waste organic matter removing calcium ions, which propagates healthy salt production. Evaporation ponds also create a zone for algae growth (*Dunaliella salina*) which results in commercial grades of beta-carotene at salinities greater than 200g/L (Ahmed et al., 2001). Therefore, this scenario is highly beneficial and can be applied to reducing costs and enhancing the evaporation ponds.

B. Salinity Gradient Solar ponds

Another potential synergy project is salinity gradient solar ponds, which combine solar energy to produce thermal energy at temperatures from 50 to 90^0C or electricity (Svensson, 2005). A normal salinity gradient solar pond comprises three regions; the top one is the surface or upper convective zone (UCZ) that has ambient temperatures and low salt content. The middle section is the main gradient zone (MGZ) or non-convective zone (NCZ) which is made up of a layer of thermal insulation and salinity gradient. The lower section is the storage zone or lower convective zone (LCZ) which is a homogenous concentrated salt solution that can be heated or remain at a stable temperature (Masnoon and Glucina, 2011). The solar energy reached at the lower zone

is released through conduction. Heat conductivity in the water is low so if the insulating layer is thick enough, heat loss will be minimal. The high volume of water in the solar pond has a corresponding high heat capacity making it ideal for energy collection and long-term storage. The temperature required to run the generation of electricity efficiently is above 85 ^{0}C. Moreover, the clarity of the brine, the thicknesses of the zones, the salt gradient and the maintenance of the vertical salt gradient and the pond area all determine the thermal efficiency of the solar pond (Svensson, 2005). A salinity-gradient solar pond can be an effective and environmentally friendly heat/cooling source for thermal desalination and brine concentration processes (Lu et al., 2002).

3.2.5.2. Crystallisers

The final phase of brine disposal in zero liquid discharge systems is the brine crystalliser method. In this process, the rejected brine is converted to a high purity water for further use in the plant while the solid masses are disposed of in landfills. The volume of brine prior to being fed to the crystalliser is minimised and is then fed to the crystalliser with a TDS concentration of approximately 200,000 – 300,000 mg/L. The first stage of crystallisation is the feeding of brine into the crystalliser, which is combined with the recirculating brine and then pumped into a heat exchanger where compression and saturated steam heats brine above boiling point at atmospheric pressure while steam condensation occurs outside the tubes of the heat exchanger.

The heated brine is then fed to a separator chamber (flash tank), at reduced pressure causing flash evaporation of the liquid and creation of insoluble salt crystals in the brine. The majority of the brine is pumped back to the heater leaving a trickle (1-5% of brine) from the recirculating loop which is sent to the centrifuge where it is filtered separating the water from the crystals enabling it to be returned to the feed tank while the solid mass is disposed of. The steam from evaporation is filtered through a mist eliminator before going into a vapour compressor where it is heated with a hot distillate and fed to a heat exchanger that heats the internal recirculating solution within the heat transfer tubes. The final process is the collection or mixing of condensed water with RO product water.

This method is the most expensive compared to other methods of brine management although has an excellent recovery rate of 95-99%, (Masnoon and Glucina, 2011; Carollo, 2009). However, a study by Mickley (2006) reveals that although costly in terms of construction, it is the most feasible method in regions that cannot support deep well injection treatment but have low solar evaporation rates. This method requires high levels of energy (200-250 kwh/1000gal) and is also commonly used with RO plants (Mackey and Seacord, 2008).

3.2.5.3. Spray dryers

An alternative method of crystallisation is the use of spray dryers, which are operated alongside a brine concentrator evaporator in desalination plants. A large cylindrical drying chamber with a dried brine separator is used to accommodate the dried solids. Meanwhile, the brine is pumped into this chamber in the form of a droplet through brine atomiser, which comprises a shaft and rotating disc protruding into the heated gas stream. In addition, hot air produced by gas, oil or electric power heater flows to the top of the drying chamber. It is then drawn into the chamber via filtration from an exhaust fan. The dry powder residue from the drying chamber is separated from the hot air stream and then prepared for disposal while the air is expelled from the atmosphere. This method is considered to be labour intensive and costly, and tends to be more effective for smaller volumes of brine (1-10 gpm) (Spellman, 2016; Masnoon and Glucina, 2011).

3.2.5.4. Wind Aided Intensified Evaporation

A more recent technology for brine treatment is Wind Aided Intensified Evaporation (WAIV), which is used to improve evaporation rates and to minimise the surface area required (Katzir et al, 2010; Masnoon and Glucina, 2011). Vertically mounted structures are erected that have wetted surfaces packed in high density footprints, which are designed to react against air movement, are placed in rows to optimise the process of using wind power. The hydrophilised ‘sails’ are made of woven netting, or other geo-textiles, or volcanic rock. Water is pumped from a nearby small storage tank to reach the vertical surface before gravity causes it to trickle down while dry air causes evaporation thereby depositing salts on the surfaces. The excess recirculates to the pond, while the salt deposits flurry and are collected in a trough below the fabric.

This method is a favourable option in terms of minimal energy requirements and reduced land area requirements, as proved in a study by Girlon et al., (2003) confirming it 20 times more effective than conventional evaporation ponds.

3.2.5.5. Dewvaporation

Another approach in dealing with small-scale applications is a cheaper option of dewvaporation which involves a thermal distillation process of desalination where dew is formed after evaporation using combustible fuel, solar or waste. The effluent disposed from this system can be almost eliminated (90%) while producing high purity distillate. A compartmentalised tower is separated by a heat transfer wall, one for dew formation and one for evaporation. Air used as a gas to evaporate the water from brine feeds forms condensation at atmospheric pressure. This air is forced at an ambient temperature to the bottom wall of the evaporation vessel while the heat transfer wall is soaked with brine by pumping it to the top of the evaporation vessel. The rise of upward-flowing heating air results in evaporation of water from the brine. Subsequently, the residue water or salt concentrate is expelled while the warm saturated air continues to rise and then goes to the condenser side of the heat transfer wall. The cooling downward air starts to condense which releases further heat via the heat transfer surface. High purity water flows out while the concentrate is collected and sent for further treatment. An advantage of this process is a lack of any scaling problems, low operating capital costs and small footprint. The downside is the large heat transfer area requirement. Although extensive piloting has been carried out, there is no full-scale application of this process for desalination and RO concentrate treatment in existence (Masnoon and Glucina, 2011; Hamieh et al., 2001).

3.2.5.6. Salt Recovery Salt Solidification and Sequestration (SAL-PROC)

Geo-Processors are responsible for a new emerging technology called SAL-PROC, which achieves ZLD by merging sequential reaction and evapo-cooling stages in a closed loop to precipitate and crystallise valuable minerals contained in brine avoiding use of any toxic elements in the process (Neilly et al., 2009). The end product of this method is a purified chemical salt of commercial value, such as magnesium carbonate, calcium carbonate and gypsum, depending on the elements contained therein

(Masnoon and Glucina, 2011). This method is used in conjunction with RO techniques and other volume reduction technologies to capitalise on the reduced need for brine disposal while producing greater amounts of potable water. Having access to inexpensive energy sources will bring costs down (Svensson, 2005). Another advantage of implementing this process is that it can recoup profits from commercial products. The downsides are that one of the main considerations of SAL-PROC systems is a requirement for sophisticated infrastructure criteria in addition to leaving a footprint to accommodate chemical reagent and product salt storage (U.S. Department of the Interior Bureau of Reclamation, 2009). The advantages and disadvantages of the aforementioned methods are summarised in (**Table 3.1**)

Table 3. 1: Advantages and disadvantages of common brine treatment and disposal methods

Disposal method	Advantages	Disadvantages
Surface Water Disposal / Direct Discharge, including tidal rivers, streams, lakes, ponds and coastal waters, such as oceans, estuaries, and bays	• No restriction on scale requirements, economically viable and widely used for disposal from high capacity desalination plans (Xu et al., 2013; Balasubramanian, 2013 ; Masnoon and Glucina, 2011)	• Bureaucratic and costly regulations, thermal contamination, loss of oxygen in ambient water, eutrophication, rise in levels of pH, impact on marine life, and its low tolerance to this increase. • Training and awareness raising needed to educate on disposal methods and their knock-on effect (Xu et al., 2013; Balasubramanian , 2013)
Discharge to outlet of the power plant	• Minimal energy use when brine is disposed from brine station alongside power plant, also reducing environmental damage (Masnoon and Glucina, 2011)	• Requires close proximity to thermal power plant (Masnoon and Glucina, 2011) • Salinity levels of ambient seawater rise as a result of continuous discharge from both plants (Uddin, 2014).
Discharge via wastewater treatment plant	• Widely recognised methods that are uncomplicated without incurring unnecessary expense or power (WHO, 2007; Masnoon and Glucina, 2011)	• Recycling of treated water for irrigation of crops with a high TDS tolerance are restricted (Masnoon and Glucina, 2011; WHO, 2007). • Feasibility subject to smaller amounts and minimal levels of TDS, currently limiting this option (Abdul-Wahab and Al-Weshahi, 2009; Voutchkov, 2014)
Discharge to sewage system	• Currently operational across well established plants with minimal overheads and power demand, used for both brackish water and wastewater (Xu et al., 2013; Masnoon and Glucina, 2011; Balasubramanian , 2013)	• Restricted to small-scale plants because of demands of hydraulic waste infrastructure and subsequent control of receiving seawater collection system, thus affecting onward irrigation use as a result of increased TDS and salinity levels (Masnoon and Glucina, 2011).
Deep Well injection		• Groundwater and subterranean earth can lead to increased salinity (Balasubramanian , 2013)

	• Can be used on mainland without any damage to the marine environment (Xu et al., 2013; Balasubramanian , 2013)	• Restricted to localised conditions and not economically feasible for small plants because of potential maintenance expense (WHO, 2007).
Land Application/Spray irrigation	• User friendly, low operating costs with optimum concentrate usage, providing excellent option for municipal use without any environmental implications, particularly on the marine biota (Xu et al., 2013; Balasubramanian , 2013).	• Inapplicable for high volumes of brine, high physical demand, harmful to vegetation, impact on salinity levels of groundwater and subterranean soil, susceptible to climate and agricultural demands (Xu et al., 2013; WHO, 2007; Balasubramanian , 2013)
Landfill Disposal	• Environmentally friendly option as a method of industrial waste disposal (U.S. Department of the Interior Bureau of Reclamation, 2009).	• Potential problems of disposing liquid waste and increased charges of storing liquid waste in drums. • Landfill sites are bound to store a minimum of 50% solid material which restricts amounts of liquid they can accept. • Cost of logistics and bureaucracy are high. • Wide variation of landfill charges (U.S. Department of the Interior Bureau of Reclamation, 2009). • Potential leakage into groundwater, subject to landfill design (Younos, 2005).
Zero liquid Discharge		
Evaporation ponds:- ✓ Aquaculture ✓ Salinity Gradient Solar ponds	• Easy and versatile with low set-up costs and maintenance, economically feasible depending on land charges. When Aquaculture or Salinity Gradient Solar ponds are used in tandem with evaporation ponds, costs are reduced with improved output and potential salt production without any deleterious effects to the marine environment (Morillo et al., 2014; Xu et al., 2013; Svensson, 2005; Balasubramanian, 2013)	• Only feasible in dry, arid conditions with high evaporation rates and expansive land space, requiring stringent procedures to prevent erosion, seepage and wildlife damage. Prevention of seepage needs lines which are not always reliable and need constant maintenance (Xu et al., 2013; U.S. Department of the Interior Bureau of Reclamation, 2009; Balasubramanian , 2013).
Crystallisers	• Widely collaborated method in industrial sector producing high-quality water with minimal	• Protracted maintenance and operating costs because of mechanical complexity, large overheads, need for regular

	environmental damage (U.S. Department of the Interior Bureau of Reclamation, 2009; Masnoon and Glucina, 2011)	cleaning in complex salt waste streams (Masnoon and Glucina, 2011; U.S. Department of the Interior Bureau of Reclamation, 2009).
Spray Dryers	• Solidification of slurry to solids makes this more feasible and versatile over a wider range of areas, with added benefit of recycling of recovered product water (Masnoon and Glucina, 2011).	• Prohibitive overhead costs combined with high energy demand (> 200 kWh/1000 gal) (Masnoon and Glucina, 2011)
Wind Aided intensified Evaporation	• Intensified evaporation rates make this option favourable with lower running and maintenance costs, using sustainable energy sources, together with minimal land requirement (U.S. Department of the Interior Bureau of Reclamation, 2009; Masnoon and Glucina, 2011).	• On-going research, susceptible to climate variations, needs high evaporation rates and regular cleansing of woven surfaces with residuals needing to be removed to landfills. Currently inconclusive data on this option (U.S. Department of the Interior Bureau of Reclamation, 2009; Masnoon and Glucina, 2011).
Dewvaporation	• A simpler form of distillation producing high quality water, easier than thermal and RO plants with reasonable operating costs due to low operating temperature and atmospheric pressure. Transfer of heat from plastic walls reduces corrosion and capital overheads (U.S. Department of the Interior Bureau of Reclamation, 2009; Masnoon and Glucina, 2011).	• Not currently in use, inconclusive evidence of output and operating costs. Water recovery is reduced 30-40% (U.S. Department of the Interior Bureau of Reclamation, 2009; Masnoon and Glucina, 2011).
Salt Recovery Salt Solidification and Sequestration (SAL-PROC)	• Effortless method based on chemical scaling to recover commercial salts that makes it a good option for brackish inland waters when coupled with RO techniques (Morillo et al., 2014; Svensson, 2005; U.S. Department of the Interior Bureau of Reclamation, 2009; Masnoon and Glucina, 2011)	• Yet to be tested on an industrial scale or evaluated in terms of operating costs, can be used well with brine consisting of high levels of dissolved sulphlate , potassium and magnesium salts (U.S. Department of the Interior Bureau of Reclamation, 2009; Morillo et al., 2014)

3.2.6. Other Brine Minimization Options used for Membrane process

In addition to the techniques previously discussed, there are others that can be used to reduce brine discharge from RO plants, as outlined below:

- Brine concentrators
- Forward osmosis
- Precipitative softening/RO
- High Efficiency reverse osmosis (HERO^{TM})
- Electrodialysis and Electrodialysis Reversal Process
- Electrodialysis metathesis (EDM)
- Capacitive deionization (CD)
- Vibratory shear enhanced processing
- Seeded Slurry Precipitation and Recycle
- Two-Pass Nanofiltration
- Membrane distillation
- Two-Phase Reverse Osmosis with Intermediate Chemical Precipitation
- Two-Phase Reverse Osmosis with Intermediate Biological Reduction (Masnoon and Glucina, 2011; Sethi et al., 2006)

3.3. Mediterranean Legislation of brine discharge from desalination plant into the marine environment

The process of desalination across the Mediterranean region is regulated by European Union water policy directives as well as Water Framework Directives (WFD). The focus of the latter is to monitor and maintain "good" water quality standards but there is a lack of regulation and guidelines to manage brine disposal into seawater on the coastal shores. The European Union knowledge that there is a certain element of damage caused by changes in salinity levels but it is not considered to be any major threat. Their only specific guidelines are for safe disposal of brine in underground aquifers, which limits their control to underground freshwater resources. It is not permitted to inject brine directly into underground aquifers, although indirect injection is allowed, provided the brine is filtered through the ground prior to reaching the aquifers (Gibbons et al., 2008).

Following the Barcelona Convention protocol in 1976 on the Protection of the Mediterranean Sea against Pollution from Land Based sources (LBS Protocol), it was revised in March 1996 by the UNEP. This protocol issues legal guidelines over the handling of marine contamination, with the purpose of limiting the effects of land-based activities in the Mediterranean, consisting of 16 sections. In Article 6 and 7 it

notes that any discharges from desalination plants should be within the confines of the restrictions contained within annex III to this protocol *(*Saliba, 1996). It was revealed in 2004 that according to the ratification status, only two countries out of the thirteen listed had joined the protocol yet, many of which host the most prominent desalination plants including Libya, Algeria, Bosnia and Herzegovina, Croatia, Egypt, Israel, Lebanon, Serbia and Montenegro, and Syria (UNEP, 2014).

A centre of research named the Marine Biology Research Centre was set up in Libya in 1981 to collaborate with an international organisation specialising in fisheries research (Food and Agricultural Organisation FAO-COPEMED), to ascertain the extent of pollution on the Libyan coastline, while researching the marine life and coastal ecosystems. Under the Strategic Action Programme for the Conservation of Marine and Coastal Biodiversity in the Mediterranean (SAP BIO) within the Barcelona Convention, three National Action Plans have been established by the Libyan government, which are: -

- National Action Plan for the Conservation of marine and coastal birds.
- National Action Plan on proposed new marine and coastal conservation areas and national parks.
- National Action Plan for the protection of Marine turtles and their habitats.

Although the Libyan Government acknowledges the need to focus on conservation of coastal lagoons and bays, to date no official policies have been agreed regarding the effects of brine disposal from coastal desalination plants (Haddoud, 2010). Thus it is imperative that WFD now recognise this important issue and put in practice specific guidelines for brine disposal (Palomar and Losada, 2011).

.

3.4. Water availability and desalination technologies in Mediterranean region

Several climatic factors along with water stress in the Mediterranean coastal areas (**fig 3.1**) have prompted the search to find alternative water resources, such as desalination and water reclamation for the future of water supply in the region (Xevgenos et al., 2015). Supply of conventional water resources (fresh surface water and groundwater resources) is threatened for the following reasons: (1) fall in levels of precipitation (2)

decline in river run-off - 20% drop between 1960 and 2000; (3) over exploitation of groundwater and (4) a surge in water consumption, tourism being one of the causes. In fact, tourism has brought almost 306 million annually^{-1} tourists which represents 37% of the global figure of tourists. This number is predicted to reach 500 million tourists by 2030, which will increase the annual water demand by 20% (UNEP, 2014).

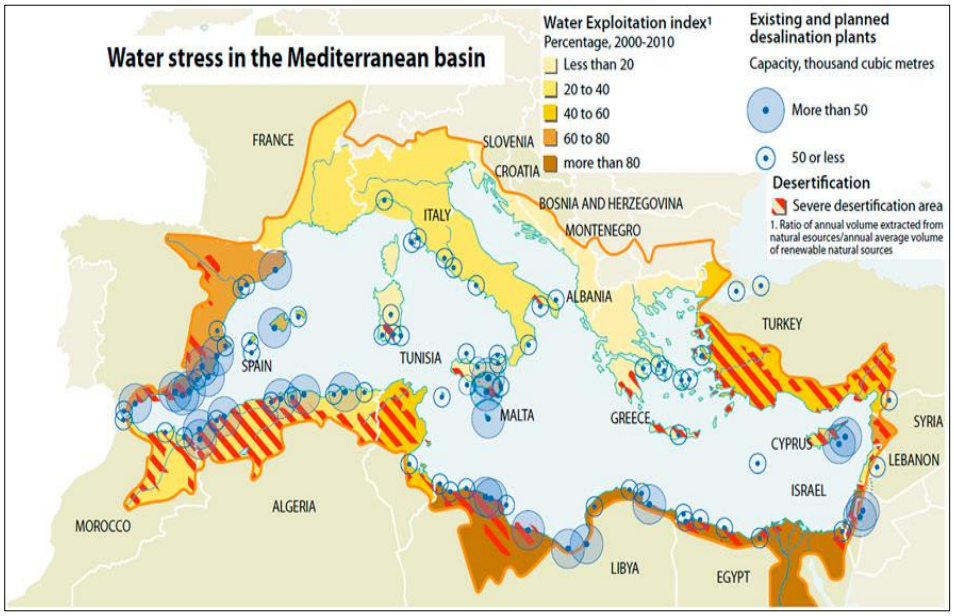


Figure 3. 1: Water Stress in Mediterranean Region (UNEP, 2014)

It has been forecast by the International panel on Climate Change that in areas like the Mediterranean, water supply will be severely affected due to climate change and global warming. As a result, there is an increase in the number of countries in the region looking for alternatives for the provision of safe water supply such as desalination (Xevgenos et al., 2015). Currently, the capacity of desalination in the Mediterranean is 11,650,047 m^3/d, representing about 16% of the total installed capacity around the world. The most prominent producers include Libya, Israel, Algeria and Spain in contrast to small countries such as Malta and Cyprus. The most common technology used within the region is RO, representing about 82.37%, MSF at 5.71% and MED at 5.60%. Electrodialysis and Electrodialysis Reversal (EDR) constituted only 4.98% and 0.09% respectively while other desalination techniques had a 2.25% share of the total (fig.3.5) (Cuence, 2012).

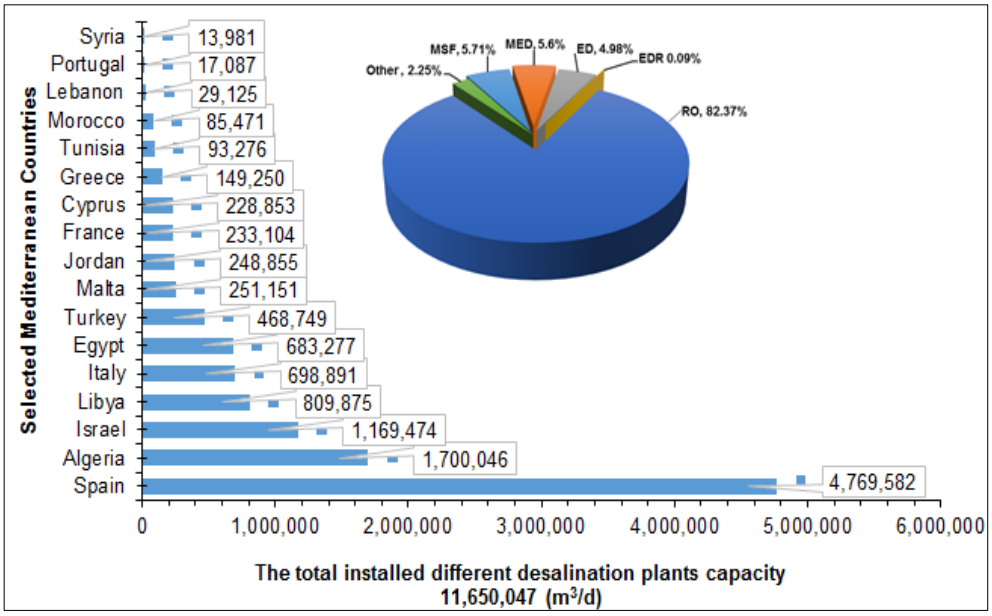


Figure 3. 2: Water desalting production capacity in selected Mediterranean countries (Cuence, 2012; Xevgenos et al., 2015).

3.5. Summary

Reject brine management poses a major environmental and financial challenge for many desalination plants so this chapter highlights the current brine management strategies, which are practised globally. The advantages and disadvantages of each technique were discussed, with considerations of potentially unviable brine disposal options such as direct discharge, discharge via wastewater treatment plants, discharge to the sewage systems, deep well injection, land application/spray irrigation and landfill disposal. They are deemed unfeasible because they can only be practised on a small scale not to mention their effects on the receiving environment.

Co-discharge of concentrate with power plant cooling water was deemed a feasible option due to cost advantages and environmental benefits of this disposal method, but the continuous brine disposal, particularly for coastal desalination plants, may increase the salinity of the ambient seawater that will affect the marine environment.

Zero liquid discharge such as crystallisers, wind aided intensified evaporation, dewvaporation, salt recovery salt solidification and sequestration (SAL-PROC) and other brine minimization options used for membrane techniques are not deemed feasible because of high costs and intensive energy demand. These technologies are still under development and are currently used to treat only small volumes of brine.

Evaporation ponds have been identified as a feasible application for concentrate disposal in arid or semi-arid places subject to land availability, such as in Libya. Furthermore, the cost of this method can be reduced by coupling aquaculture or salinity gradient solar ponds. Nonetheless, this method is ineffective in damp climates because the evaporation rate is very low. Therefore, there is still need for research of feasible solutions that can fulfil the technical, environmental and cost requirements of desalination technologies, particularly in arid or semi-arid regions, such as those countries sited in the southern Mediterranean region particularly in Libya, classified as the fourth largest user of desalination technologies. EU legislation for Mediterranean countries about the brine disposal from desalination plants into the marine environment does not contain specific regulations about the impacts of brine on the marine environment. Hence, the next chapter will evaluate the water resources availability in Libya.

Chapter Four: Available Water Resources in Libya

4.1. Introduction

The earth's surface comprises 71% water (510×10^6 km^2) and 29% land, (Shiklomanov and Rodda, 2003) but only 3% of that water is potable, the remainder being saltwater (Cooley et al., 2006). Furthermore, a huge 70% of that potable water is made up of glaciers with the remaining 30% being underground from which a mere 0.25% reaches rivers and lakes. (Kalogirou, 2005). This poses the dilemma of only having a small amount of freshwater available globally (Khawaji et al., 2008).

In fact, in 1996 the World Water Council announced that the lack of freshwater posed a very real threat to existence unless steps were taken to replenish much needed supplies for continuing economic and social development while protecting the ecosystems (Bindra et al., 2014).

Between 1955 to 1990, the population of North Africa rose dramatically from 49.5 million to 118.1 million. By 2025, this figure is predicted to rise above 188 million. The annual water volume per capita was 2,285 m^3 in 1955 and declined to 958 m^3 in 1990. It is predicted that this figure will reach 602 m^3 over the following 35 years. Availability of potable water in this area is estimated at 113.1 km^3/year, so a significant ongoing depletion of water supplies is expected in the future (Alghariani, 2007).

Across the continent of Africa, there are substantial sedimentary aquifers storing 0.66 million km^3 of water, the majority of the contents (0.44 M km^3) exist over eight Saharan nations including the Nubian Sandstone, which supports Libya, Sudan, Egypt and Chad. Owing to the depth of the aquifers in Libya at 2.5km thick, the cost of deploying required processes is high. (MacDonald et al., 2012).

Libya has been classified as one of the ten most inadequate water source suppliers and since 1970, the country has suffered severe water scarcity (Abughlelesha and Lateh, 2013) Thus, the provision of water has been high on the agenda to meet increased population, not to mention other demands from all sectors (Wheida and Verhoeven, 2007). As a consequence of these demands, several coastal groundwater aquifers have become contaminated with seawater, causing water in the aquifers to become brackish.

This has posed serious concerns, particularly in agriculture, where a combination of low rainfall (Bindra et al., 2010; Wheida and Verhoeven, 2007) and gradual penetration of saltwater into coastal aquifers has contributed to damaging natural groundwater sources. Thus, it has become incumbent on the Libyan government to focus on various projects that can resolve the increased demand for water in different sectors, such as desalination technology (Elabbar and Elmabrouk, 2005).

As a result of water scarcity and the imbalance between water resources in Libya and demand, this chapter aims to assess the existing water resources in Libya and the impact of population growth on the available water resources in the country. It will also give the context of current water infrastructure, the supply and demand and the ongoing challenges. Finally, this chapter is intended to expose the water deficit across Libyan regions while also comparing the cost of water produced by the Great Man-Made River Project with a thermal desalination plant by using the Abotraba desalination plant as a case study.

4.2. Study site

Libya is situated in the heart of North Africa between 17 longitude east and 26 latitude north; It's on the southern shores of the Mediterranean Sea (fig 4.1) which has a coastline of approximately 2,000 kilometres (Hamad et al., 2014). It borders Sudan and Egypt to the east, Chad, Sudan and Niger to the south and Tunisia and Algeria to the west. Its total land mass is 1.8 million square kilometres, it is classified as being the seventeenth largest nation in the world and the fourth largest African country. In terms of overall size, it is seven times the size of the United Kingdom (Tamatm et al., 2011) having 94.5% of its land area as desert (Bindra et al., 2013).

Its gross domestic product is comprised mainly of oil and gas, and it is the fifth most important supplier globally, giving it an important strategic position as a trading supplier across Europe (Mohamed et al., 2015; Khalil and Asheibi, 2015).

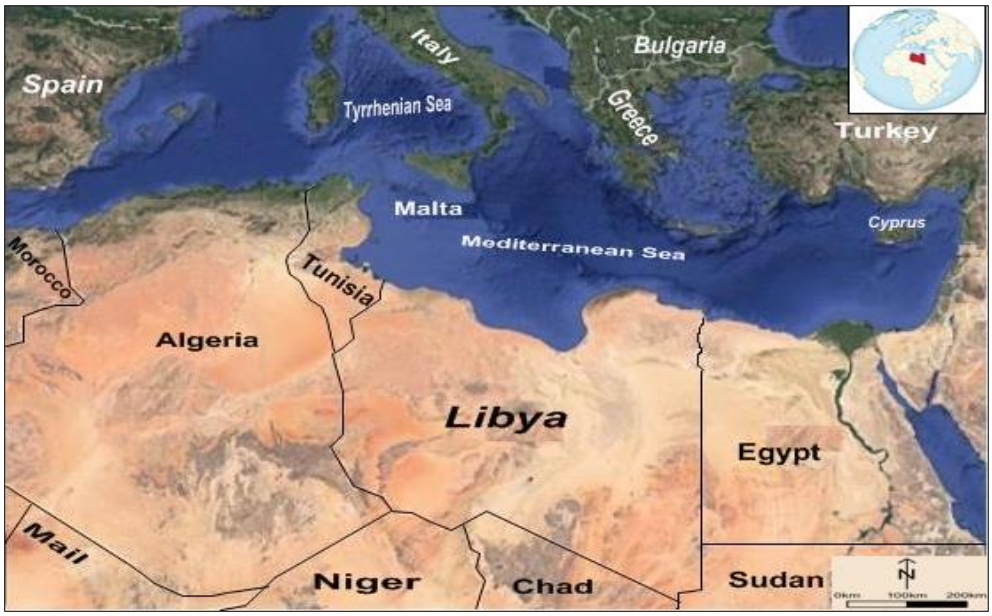


Figure 4. 1: Location of Libya (Google earth, 2016) (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

4.2.1. Population growth rate in Libya

The Libyan Bureau of Statistics and Census (LBSC) is responsible for measuring changes in population in Libya by undertaking population surveys every decade as conducted between 1972 and 2012 (Table 4.1) (Bureau of Statistics and Census Libya, 2013). The population growth rate equation was applied as written by (Sujay, 2012) to evaluate changes occurring over time.

$$\mathbf{PGR} = \left(\frac{\boldsymbol{Population\ in\ present}}{\boldsymbol{Population\ in\ past}}\right)^{\frac{1}{n}} - \mathbf{1} \quad \ldots\ldots\ldots\

4.2.2. Water resource management in Libya

Government policies regulating water supply are formulated at different levels. Each body has a responsibility to stipulate conditions relating to public and national water supply, considering implications of waste and subsequent damage to the environment as well as protecting and managing the water sources across the country. There are six such authorities across different sectors that are responsible for managing water resources in Libya.

4.2.2.1. General Water Authority (GWA)

In 1972, the General Water Authority was set up as a major independent body to oversee all matters pertaining to water, but was subsequently established as the Ministry of Dams and Water Resources, specialising in agriculture in 1979. Later, in 1991, it was run by an appointed committee as a Ministry of Agriculture. In the early 90's the government focussed on a range of projects relating to water supply pipe networks, sewage systems and other necessary infrastructure developments which ultimately led to the establishment of the General Water and Sanitation Company (GWSCo) in 1997, supervised by the Municipal Secretary. Within this organisation are five offices covering whole cities across the country, such as Benghazi, Sirte, Tripoli, Sabha and Gharyan. After the establishment of the GMMR network project, this authority extended their responsibilities by employing specialists to deal with hydrogeology sciences, civil engineering applications, agriculture and other water-related matters. The duties of these specialists included authorising, managing and regulating any water-related projects, provision of wells drilling licences, maintenance of groundwater wells, design and construction of dams, water-soil investigation studies, and supervision of RO practices inland and on the coastline. They regulated changes in quantitative and qualitative conditions of water resources while ultimately influencing government policy on national water resources (General Water Authority, 2011).

- **Challenges**

Since the revolution in Libya, there have been several challenges posed that have threatened the ongoing projects that had been established prior to 2011. Several of the existing water pumping stations and desalination and waste water treatment plants had

gone into decline due to lack of maintenance or skilled operators, combined with loss of investment and finance. Following sanctions, import of specific parts required was stopped, causing plants to become neglected and dilapidated, resulting in a loss of credibility with economic partners (Senoussi, 2012).

4.2.2.2. Great Man-Made River Authority (GMMRP)

The Great Man-Made River Authority was established in 1983 for the purpose of extracting water from deep aquifers located in the South and conveying it to the North in the most practical and economically viable way, for consumption in the Libyan coastal areas. This authority is in charge of five phases of implementation that include establishing plans. In addition, they are involved with all technical research and data required for operation. In order to deal with large volumes of water to be consumed by different sectors such as municipal and industrial but mainly for agricultural needs, it was necessary to liaise with other relevant stakeholders to distribute water from the project to all concerned (Great Man-made River Authority, 2012).

- **Challenges**

Following the revolution in Libya, lack of spare parts, financial deficits and delays in completion of work orders have been some of the challenges facing the authority. Other problems such as poor condition of pipe networks, disinfection and water pumping stations combined with lack of maintenance of deep aquifers, have added to these issues (Alhabishe, 2012).

4.2.2.3. Electricity and Renewable Energy Authority (GECOL)

This was a government authority created in 1984 as an independent body known as General Electric Company of Libya (GECOL), responsible for constructing the national grid in the form of major steam and gas power stations, electric control centres, feed plants, and provision of electricity for national consumption. This authority was responsible for the provision of industrial water by the construction of desalination plants in cooperation with steam power stations, due to higher consumption by certain sectors such as industry, agriculture and domestic use. Before 2010, the majority of such desalination plants had been under the control of this government authority, which was in charge of design, signing contracts with the main

construction companies and subsequent management of these stations. However, after 2010, a resolution decreed that GECOL were to be only responsible for their own desalination plants for provision of potable water for residential and industrial consumption, leading to the establishment of the General Desalination Company of Libya (General Electric Company of Libya, 2015).

- **Challenges**

Prior to the revolution, there had been regular maintenance of power stations, but since 2011, there have been major challenges affecting regular supply of electricity with frequent blackouts impacting on continuing maintenance and re-building of further desalination plants that work with power plants. As mentioned earlier, shortages of spare parts, combined with financial restrictions and trading partners has resulted in compromised operating standards of desalination plants (Abulqasem, 2012).

4.2.2.4. General Desalination Company of Libya (GDCOL)

This authority took over the previous responsibilities of GECOL to regulate the larger capacity coastline desalination plants for the provision of freshwater. Its main function was to produce non-conventional water sources and deliver potable water to all Libyan cities located close to the coastline. They were also responsible for signing any new contracts, designing network piping, and managing coastline desalination plants while maintaining full compliance with legal, health and safety and environmental criteria (General Desalination Company of Libya, 2013).

- **Challenges**

Following the revolution, several international companies that had previously been involved in installation, expansion and maintenance of desalination plants were forced to relinquish their responsibilities due to the situation in Libya. Furthermore, the local authorities faced challenges due to lack of spare parts, finance, skilled labour and cessation of capacity building of existing plants (Sidon, 2013).

4.2.2.5. National Oil Corporation Authority (NOC)

In 1970 the Libyan General Petroleum Corporation Authority was replaced by the National Oil Corporation, which had been established in 1968. Their function was to

continue the exploitation of oil reserves for the purposes of providing and optimising the main source of power to the country to support the national economy (National Oil Corporation, 2014). Due to lack of water in the country, their role was to provide potable water for residential consumption and industrial water to service the oil fields by constructing desalination plants as a water supply. This authority was also responsible for the design and construction of seawater and brackish water desalination plants working in the oilfields (Al-Hengari et al., 2015).

- **Challenges**

Following political turmoil after the Libyan revolution, this authority has been unable to continue at the same capacity because of loss of skilled workforce, lack of maintenance and safety procedures that have all contributed to a decline in the operation of desalination plants working within the oilfields (**Al-Hengari et al., 2015**).

4.2.2.6. General Environment Authority (GEA)

Following environmental laws established in 1982 to protect the environment, this authority was established in 2000 as an independent body by monitoring and regulating industrial, agricultural and domestic activities (General environment Authority, 2011). They were responsible for monitoring the operations of the five organisations (**fig 4.2**).

In addition, they put in place awareness raising initiatives that educated the public about the consequences of pollution of the ecosystem while ensuring sustainable development. This involved regular inspections to prevent any activity that could be deemed damaging or toxic to the environment (General environment Authority, 2011).

- **Challenges**

After the revolution, the challenges facing this authority included reduced monitoring and inspection due to reduced workforce, financial problems and overall management of authorities (Mohamed, 2013).

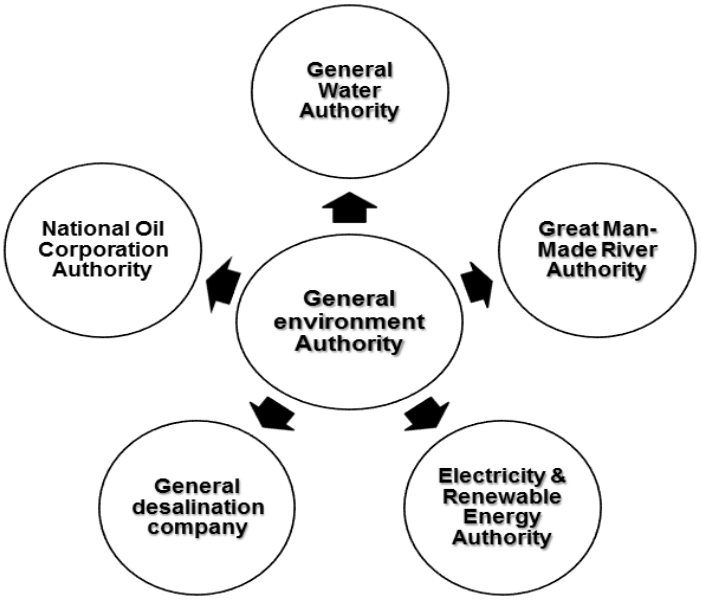


Figure 4. 2: The administrative structure of water resources management in Libya

4.3. Water resources available in Libya

According to a geographical survey, water resources in Libya are divided into five different water regions (**fig 4.3).**

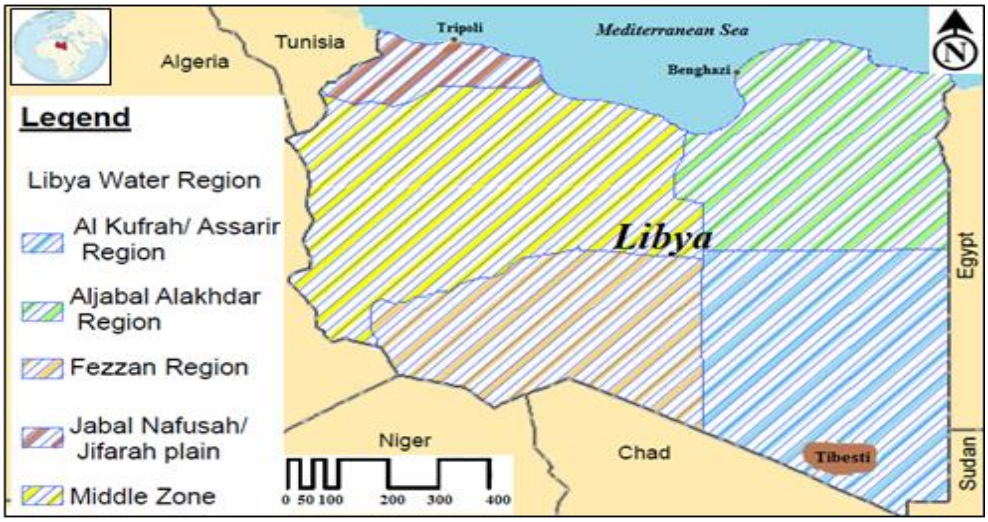


Figure 4. 3: Water regions in Libya (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

4.3.1. Groundwater

Groundwater is found in two types of aquifers, namely shallow aquifers with approximately 600 million m^3/year water production (Abdudayem and Scott, 2014),

and deep aquifers (artesian aquifers) containing unsustainable fossil water. Water production and the types of groundwater reservoirs differ according to regions.

4.3.1.1. Jabal Nafusah and Jifarah Plain water region

Cultivation in this more densely populated northwest region thrives due to good quality soil. In this location, aquifers are of Cretaceous/Triassic formation. Approximately 350 m^3/hr is discharged from artesian aquifers in contrast to 2-3 m^3/sec from shallow wells (El Asswad, 1995). An estimated annual amount of 250 million m^3/year constitutes total water production (Abdudayem and Scott, 2014) with an annual deficit of approximately 1,450 million m^3 (El Asswad, 1995). Due to seawater incursion in this region, the amount of dissolved solid varies between 1,000-5,000 ppm (Wheida & Verhoeven, 2006; Abdudayem and Scott, 2014).

4.3.1.2. Middle zone

The middle zone lies between Fezzan and Alharuj Asward to the south, Jifarah Plain to the west and Aljabal Alakhdar to the east (El Asswad, 1995; Abdudayem and Scott, 2014), where water consumption is approximately 400 million m^3/year (Abdudayem and Scott, 2014) with an estimated deficit of 250 million m^3 /year. The reservoirs are shown to be of tertiary quaternary formation, drilling has been carried out along the coastline on the shallow aquifers (El Asswad, 1995), According to Wheida & Verhoeven, 2006; Abdudayem and Scott, 2014 dissolved solids in the deep wells total anything between 1,000-5,000 ppm.

4.3.1.3. Aljabal Alakhdar region

This area borders Egypt to the east and constitutes the coastal belt and north eastern regions, including Benghazi Plain across to the Aljabal Alakhdar zone. The water deficit in this location is approximately 60 million m^3/year (El Asswad, 1995; Wheida & Verhoeven, 2006) with an estimated water supply of 250 million m^3/year (Abdudayem and Scott, 2014). In this location, reservoirs are of tertiary limestone formation above an impermeable line of late Cretaceous rock formation (El Asswad, 1995), with dissolved solids ranging from 1,000-5,000 ppm (Wheida & Verhoeven, 2006; Abdudayem and Scott, 2014).

4.3.1.4. Fezzan region

In this region situated in the southwest of the country, ground water is collected from two aquifers, one which is of Devonion and Cabro-Ordovician extract, the other is formed from the early Cretaceous/Triassic period, made of Nubian sandstone. No water supplements the existing groundwater due to scarcity of rainfall, although according to water balance indicators, there is some existing ground water in the area of approximately 515 million m^3 (El Asswad, 1995; Wheida & Verhoeven, 2006) Research has revealed that there is a huge quantity of underlying ground water situated in a deep layer beneath. The artesian aquifers produce approximately 1,800 million m^3/year with total dissolved solid ranging from 200-1,500 ppm (Wheida & Verhoeven, 2006; Abdudayem and Scott, 2014).

4.3.1.5. Al Kufrah and Assarir region

This region is located in southern and eastern Libya, the amount of dissolved solids ranges from 0.5-3.5 ppm (Wheida and Verhoeven, 2006; El Asswad, 1995). There are two aquifers in this area; one of tertiary sandstone formation close to Assarir, the other is situated in the centre of Al Kufrah basin, made of Nubian sandstone. Annual water consumption is estimated at 1,500 million m^3/year with a surplus of approximately 1,110 million m^3. The Great Man-Made River project (GMMRP) conveys 6.18 million m^3/day of all the fossil water through a network of pipes to the northern region (fig 4.4) (El Asswad, 1995).

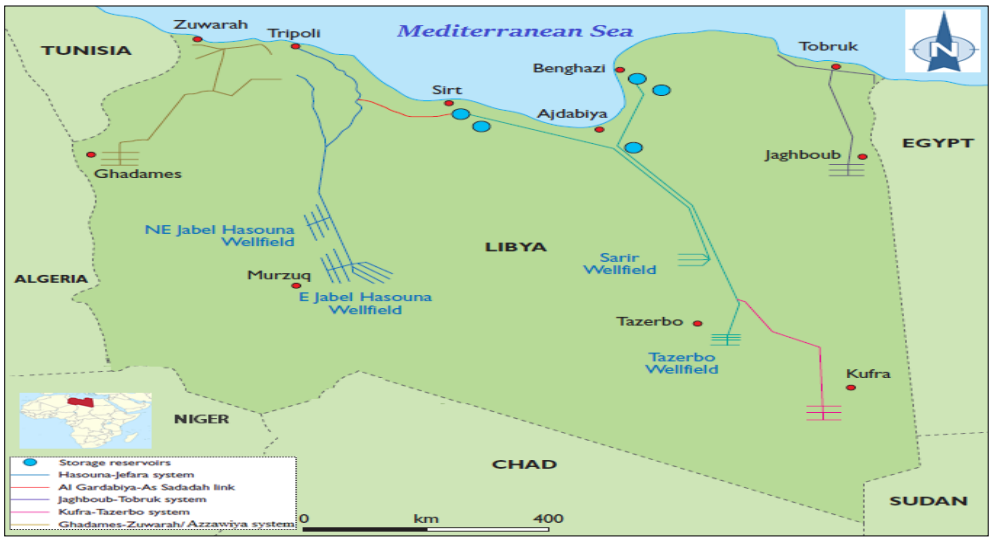


Figure 4. 4: Great Man-Made River Project in Libya (Kuwairi, 2006) (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

This five-stranded project was initiated in the mid-1980's and is an ongoing development (Al habashi, 2012). Part one set out plans to distribute 2 million m^3/day of fresh water from south eastern basins in Tazerbo and Sarir across to the north eastern cities of Benghazi and Sirte through pre-stressed concrete 4m diameter concrete pipe lines (Kuwairi, 2006) with an annual discharged constant flow of 700 million m^3 (Wheida and Verhoeven, 2006). Out of the anticipated water production from this stage, 410,170 m^3/day was destined for municipal use, 1,506,030 m^3/day for agriculture and 83,800 m^3/day allocated for industry (Middle East business intelligence, 2010).

In the second stage, it was planned that 2.5 million m^3/day of fresh water would reach Tarhouna and Tripoli (Abdelrhem et al., 2008) from East Jabal Hasouna and North East Jabal Hasaouna well fields. Similarly, water was passed through pipe lines originating from the well field, split into two parts for the purpose of reinforcing the first phase that was prone to collapsing wells and affected by the reduced number of coastal aquifers on the coastal belt. In this second phase, 1,316,090 m^3/day was allocated for municipal use, 1,175,660 m^3/day for agriculture and 8,250 m^3/day directed to industry (Middle East business intelligence, 2010).

While the third phase was still in progress, there was a plan to build a pump station at Kufra well field with 380 km of pipeline connecting Tazerbo to Sarir for the purpose of distributing a further 1.68 million m^3/day of fresh water of which 253,000 m^3/day was destined for municipal use and 1,427,000 m^3/day for agricultural use, excluding the industrial sector (Middle East business intelligence, 2010). The last two phases are still ongoing and will focus on the construction of a pipeline from Gadammes to connect northwards towards the coastal areas of Zwuarah and Azzawiya.

The fifth phase proposes to construct a pipe network from Jagboub oasis going eastward to Tubruk (Wheida and Verhoeven, 2006). A total of 5,000 kilometres of network pipes was used by GGMR, originating from 1,261 wells that had been drilled from 450 m up to 800 m with reservoir storage capacity reaching 54.9 million m^3 (Middle East business intelligence, 2010; Salem, 2007) (Table 4.2).

Table 4. 2: Location of wellfields and reservoirs of GMMRP (Middle East business intelligence, 2010)

Location of wellfields	Number of wells
Ghadames system	106
Northeast Jabal Hassouna system	60
East Jabal Hassouna system	479
West Jabal Hassouna system	47
Brega pipe manufacturing plant, water system	7
Sarir pipe manufacturing plant, water system	3
Sarir wellfield system	126
Tazerbo wellfield	108
Kufra system	285
Jaghboub	40
Location of reservoirs	**Design capacity**
Ajdabiya holding reservoir	4
Al-Gardabiya reservoir	6.8
Omar Mukhtar reservoir	4.7
Grand Al-Gardabiya reservoir	15.4
Grand Omar Mukhtar reservoir	24

4.3.2. Surface water

Climate conditions in Libya are typically Mediterranean along the coastline whilst inland temperatures can reach 50^0C in the heat of summer but it is more likely to be around 40^0C elsewhere. The average rainfall ranges from 200-500mm in Jabal Akhdar known as the Eastern Highlands to 750-800mm in the western area of Jabal Nafusah known as the Western Highlands (Zeleňáková et al., 2014). In the southern regions such as Kufra, Murzek and Sarir, these levels fall dramatically with barely any rainfall (Abdudayem and Scott, 2014). Over a period of a year, the average temperature is 20.5^0C (Hamad et al., 2014).

The annual rainfall in Jifarah Plain and Jabal Nafusah, the Middle Zone, AljabalAlakhdar and Fezzan area was approximately 197 million m^3 in contrast to natural springs yearly flow at 184 million m^3 (Dimkic et al., 2008). This reduces the productivity of the shallow aquifers, which rely on rainfall and trickled water. Following the construction of dams with a capacity up to 389.89 million m^3/year, surface water resources have flourished.

However, due to lack of maintenance and scarcity of rain, the existing storage capacity was reduced to approximately 61.35 million m^3/year (Table 4.3) (Abdudayem and Scott, 2014).

Table 4. 3: Dam capacity in Libya (Abdudayem and Scott, 2014)

Water Region	Dame name	Location	Designed storage capacity ($10^6 m^3$)	Existing storage capacity ($10^6 m^3$)
Jabal Nafusah and Jifarah Plain	Wadi Mejnean	Ben-Gashir	58	10
	Wadi Ghan	North Gharyan	30	11
	Wadi Zart	Rabta	8.6	4.5
Middle zone	Wadi Ekaamm	Zliten	111	13
	Wadi libda	Homes	5.20	3.4
	Wadi Tibreat	Zliten	1.60	0.5
	Wadi Edkaar	Zliten	1.60	0.5
Aljabal Alakhdar	Wadi Qattara	Benghazia	135	12
	Wadi Qattara-2	Bengazia	1.50	0.50
	Mrks	Ras-hlal	0.15	0.15
	Zara	Aloqurea	2	0.80
	Derna	Derna	1.15	1
	Abomansour	Derna	22.30	2
Kufra/as-Sarir	Garif	Sirt	2.40	0.30
	Zhawia	Sirt	2.80	0.70
	Ziud	Sirt	2.60	0.50
	Benjuid	Benjuid	0.34	0.30
	Wadi Zgar	Jufarh	3.65	0.20
Total storage capacity (million m^3)			**389.89**	**61.35**

4.3.3. Wastewater treatment plant

There has been mixed reactions to the construction of wastewater treatment plants in Libya since the 1970's (Abdudayem and Scott, 2014) due to a huge growth in the population along with urbanisation particularly on the Libyan coastline. Consequently, there has been a need to improve the infrastructure to support the growing population, including the development of highways, waterworks and sewage plants in both central and outlying areas. The latter was prioritised as a matter of public safety and for environmental impact. Furthermore, it necessitated investment in non-conventional water resources for other sectors, such as in agriculture (Wheida & Verhoeven, 2006). Indeed, in 1998, 6,000 hectares of agricultural land was irrigated by treated wastewater in Benghazi and Tripoli (Table 4.4) (Abdudayem and Scott, 2014).

Table 4. 4: Agricultural areas irrigated by wastewater treatment plants (Abdudayem and Scott, 2014).

Project location	Stage	Discharge capacity, m^3/day	Irrigated area, hectare
Tripoli	**1st stage**	**27,000**	**2500**

	2nd stage	**110,000**	**1500**
Benghazi	**1st stage**	**27,000**	**360**
	2nd stage	**27,000**	**658**
	3rd stage	**27,000**	**1000**

Over 30 wastewater treatment plants (WWTPs) (fig 4.5) were constructed along with approximately 6,000 kilometres of sewage collection and transport pipelines. Currently, several plants are in the process of being constructed to serve about 400 inner cities and semi-urban areas (Cedare, 2014). Less than half the population (45%) consumes water from secondary/tertiary wastewater treatment plants in contrast to 54% from rural and urban areas who are served with septic tanks and on-site decentralised units that are not regulated by the water authority (General Water Authority, 2011).

Figure 4. 5: Location of WWTPs in Libya

According to the Bureau of Statistics and Census Libya 2012, there are only 9 WWTPS that run to optimum standards. Between the years of 1963 and 2009 across major cities, the design capacity of established larger plants reached 677,735 m^3/day in contrast to existing levels of 66,233 m^3/day (General Water Authority, 2011) (Table 4.5). This is a result of reduced monitoring, checking and evaluation of plants some of which were not checked at all. In 2007, a plan was put in place for the development of a wastewater treatment plant but no mention was made as to whether it was for domestic and/or agricultural purposes.

Table 4. 5: Design and Existing wastewater treatment plants in Libya between 1963-2009 (Abdudayem and Scott, 2014).

Treatment Plant	Installation Year	Design Capacity (m^3/day)	Existing Capacity (m^3/day)	Remarks
Ejdabya	1988	15,600	5,000	-
Benghazi A	1965	27,300	-	Out of order
Benghazi B	1977	54,000	-	Provisional test
Al-merg A	1964	1,800	-	Out of order
Al-merg B	1972	1,800	-	Out of order
Al-beada	1973	9,000	-	Under construction
Tubruk A	1963	1,350	-	Out of order
Tubruk B	1982	33,000	-	Out of order
Derna	1965	4,550	-	Out of order
Derna	1982	8,300	-	Under construction
Sirt	1995	26,400	-	Under construction
Abo-hadi	1981	1,000	600	-
Al-brega	1988	3,500	2700	-
Zwuarah	1980	41,550	-	Out of order
Sebrata	1976	6,000	-	Out of order
Sorman	1977	20,800	-	Under construction
Azzawiya	1976	6,800	-	Under construction
Zenzour	1977	6000	-	Not used
Tripoli A	1966	27,000	-	Out of order
Tripoli B	1977	110,000	20,000	-
Tripoli C	1981	110,000	-	-
Tajoura	1984	1,500	500	-
Tarhouna	1985	3,200	1,260	-
Gharyan	1975	3,000	-	-
Yefren	1980	1,725	173	-
Meslata	1980	3,400	-	-
Homes	1990	8,000	-	-
Ziliten	1976	6,000	-	Out of order
Misrata A	1967	1,350	-	Out of order
Misrata B	1982	24,000	12,000	-
East Garyat	1978	500	-	Out of order
West Garyat	1978	150	-	Out of order
Topga	1978	300	-	Out of order
Shourif	1978	500	-	Out of order
Sabha A	1964	1,360	-	Out of order
Sabha B	1980	47,000	24,000	Out of order
Ghadames - Hospital	1980	8,000	-	Out of order
Ghadames-B	2007/2009	6,0000	-	Under construction
Total Design Capacity (m^3/day)		**677,735**	**66,233**	

4.3.4. Water Desalination

Water desalination technology is a vital tool in Libya to fulfil the demands of potable and industrial consumption, particularly in view of its extended coastline and a scarcity of water sources, which the GMMRP project cannot achieve in its own right (Elabbar and Elmabrouk, 2005). By the mid 1960's desalination units were gradually established by petroleum organisations (Al-Hengari et al., 2015). Since then, Libya has embraced the use of two types of technology, thermal and membrane desalination making it one of the major users in the Mediterranean region. Due to a lack of ground

water and high contamination levels, different water authorities in the country are involved in desalination technology, such as General Desalination company of Libya (GDCOL), General Electric Company of Libya (GECOL), General Water and Sanitation Company (GWSCo), National Oil Corporation Authority (NOC), Libyan Iron and Steel company (LISCo), Industrial Research Centre of Tajoura (IRC).

The total design capacity of all desalination plants in Libya was estimated to be 847,600 m^3/day. However, the total existing water production from desalination technology has fallen to a level of 493,647 m^3/day due to low maintenance and certain desalination plants falling into decline (**Table 4.6).**

Table 4. 6: Design capacity of desalination plants in Libya

Location of station	Year of operation	Method of Desalination	Number of Unit	Capacity/ Unit (m^3/day)	Design Capacity (m^3/day)	Existing Capacity (m^3/day)	Water authority
Zwuarah	2006	MED	6	13,333.33	80,000	40,000	GDCOL
Azzawiya	2009	MED	6	13,333.33	80,000	40,000	GDCOL
Zeltin	1992	MSF	3	10,000	30,000	20,000	GDCOL
Abutraba	2006/2007	MED	3	13,333.33	40,000	40,000	GDCOL
Soussa	2009	MED	3	13,333.33	40,000	40,000	GDCOL
Derna	2009	MED	3	13,333.33	40,000	40,000	GDCOL
Khaleg Albomba	1989	MSF	3	10,000	30,000	10,000	GDCOL
Tubruk-1	2001	MED-TVC	3	13,333.33	40,000	40,000	GDCOL
Total Existing Capacity (m^3/day)						**270,000**	
Zwuarah	1975/1978	MSF	3+1	13,500+4,500	45000	O/S	GECOL
Azzawiya power station	1999	RO	2	5000	10,000	8,000	GECOL
Tripoli west-old	1978	MSF	8	6000	48,000	O/S	GECOL
Tripoli west-new	1999	MED	2	5000	10,000	7,000	GECOL
Komas	1982	MSF	4	10,500	42,000	25,000	GECOL
Zeltin-2	1978	MSF	3+1	13,500+4,500	18,000	O/S	GECOL
Zuitina-1	1983	MSF	3	10,000	30000	20,000	GECOL
Zeltin-old	1964	EDR	-	-	-	O/S	GECOL
Misrata	1984	RO	5	10,000	50000	O/S	GECOL
Sirt-1	1976	MSF	1	9000	9000	O/S	GECOL
Sirt-2	1986	MSF	1	10,000	10,000	8000	GECOL
Benjawad	1978	-	-	-	6000	O/S	GECOL
Ras-lnof	1983	MSF	3	24000	72000	O/S	GECOL
Al-Brega	1982	MSF	2	4,800	9,600	O/S	GECOL
Benghazi north	1978	MSF	8	6,000	48,000	10,000	GECOL
Soussa	2001	MED	2	5,000	10,000	8,000	GECOL
Total Existing Capacity (m^3/day)						**86,000**	
Ajeelat	2000/2003	RO	-	500		O/S	GWSCo
Sabratha-theatre	2000/2003	RO	-	500		O/S	GWSCo
Sabratha- Talil	2000/2003	RO	-	500		O/S	GWSCo
Sabratha- Al- hensher	1999	RO	-	500		O/S	GWSCo
Sorman	2003/2003	RO	-	500		O/S	GWSCo

Total Existing Capacity (m^3/day)						**0**	
Sirte Oil Company	1964/1989	MSF/MED/RO	9/3/7	-	-	22,708	NOC
Ras-Lanuf chemical complex	1983/1997	MSF	5	6000	-	30,000	NOC
The Arabian Gulf Oil Company	1999	MED/RO	2/1	-	-	750	NOC
Azzawiya Oil Refining Company	1974/2004	MSF/MED	5/2	-	-	5,500	NOC
Mersa Brega petrochemical complex	1964/1989	MSF/MED	9/3	-	-	21,387	NOC
Mellitah Oil & Gas B.V	1982/2004/2005	RO/MSF/MED&ED	5/3/11	-	-	20,340	NOC
Zueitina Oil Company	1964/2004	RO/MED/ED	7/5			532	NOC
Harouge Oil Operations	1986/2005	RO/MED/RO	7/1			680	NOC
Tubruk oil refinery		MED	2	375		750	NOC
Total Existing Capacity (m^3/day)						**102,647**	
Libyan Iron and Steel company	1987	MSF	3	1,0000	3,0000	25,000	LISCo
Total Existing Capacity (m^3/day)						**25,000**	
Abu Kammash chemical complex	1981	MSF	1	2,400	2,400	O/S	GCCI
Industrial Research Centre- Tajoura	1983	RO	2	5000	1,0000	5,000	IRC
Total Existing Capacity (m^3/day)						**5,000**	

Reverse Osmosis (RO), Electro-dialysis Reversal vapour (EDR) Multi-Effect Distillation (MED), Multistage Flash Desalination (MSF), (O/S) Out of service

The daily water production from the two main water sources including the first two stages of GMMER project and desalination plants in Libya are summarised in **(Table 4.7).**

Table 4. 7: Daily water production from different water sources in Libya

Supplier Name	Potable water (m^3/day)	Industrial water (m^3/day)	Agriculture water (m^3/day)	Total (m^3/day)
GMMR	1,726,260	92,050	2,681,690	4,500,000
Desalination Plants	382,029.4	123,871.6	0	505,901

4.4. Cost of different water sources in Libya

The main water sources in Libya are the Great Man-Made River project (GMMRP) and desalination plants so costs were examined analysing the cost of a cubic metre of water produced by GMMR against the cost of a cubic metre from a thermal desalination plant. The figures for GMMRP were dependent on previous publications, whereas those for thermal technology were based on a case study carried out at a thermal desalination plant located on the Libyan coastline.

4.4.1. Cost of a cubic metre transferred by the GMMRP

The predicted cost of the GMMRP is approximately $27.08 billion spread over three phrases, comprising an investment of $19.58 with a remaining amount of $7.5 billion allocated for investment in the fourth and fifth phases ready for completion in 2025. (Bunta, 2010). Following completion of the first phase of the Great Man-Made River project in 1991, the cost of a cubic metre was analysed to include a fixed capital cost of 7% at a price of $0.83. However, on close economic analysis during the formation of the GMMRP, it was found that the cost of a cubic metre of water conveyed from the southern area to the coastal belt was set at $0.25 (Alghariani, 2007).

4.4.2. Cost of a cubic metre Produced by thermal desalination technique (MED-TVC)

4.4.2.1. Case study

This study was conducted in September 2012 on the Libyan coastline around the Abotraba distillation plant (**fig 4.6**), which was built by a French company called

SIDEM. Abotraba was first commissioned in 2006/2007, situated in the district of Aljabal Alakhdar in the North-eastern region (N 32.648742°, E 20.824107°). Freshwater in this plant was obtained by the application of thermal energy to the seawater feed in multi effect stages with thermal vapour compression (MED-TVC) creating a distillate of fresh water while the brine stream is returned to the sea. Abotraba plant produces around 40,000 m^3day^{-1} of effluent to the marine environment of which 26,666.7 m^3day^{-1} is brine water. The main purpose of this station is to provide the cities such as El Marj, Al-Abiar, and Alakorah with fresh water.

Figure 4. 6: Case study - Abotraba desalination plant (Google earth, 2016) (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

4.4.2.2. Data collection

During the field study, data was collected from the control room and efficiency department of Abotraba desalination station in Libya.

4.4.2.2.1. Chemical additives costs

During the course of chemical treatment on MED-TVC units, a range of chemical additives are used including bio-fouling (chlorine), anti-scale, anti-foam, pH adjustment additives, sodium bisulphite and acid for cleaning as required. The estimated annual expenditure is $736,620.54 with annual water production of

12,277,009 m^3 over 2010. Therefore, the calculated cost of chemical additives per m^3 of desalted water for Abotraba distillation plant is $0.06.

4.4.2.2.2. The cost of labour

Labour costs comprise permanent staff for operation, routine maintenance and administration as well as desalination plant operators and members of management. These figures vary according to staff background and skillset. The Abotraba distillation plant employed 53 members of staff with annual salary overheads in 2010 of $98,216.1 with annual water production of 12,277,009 m^3 making the cost of labour per m^3 of desalted water for Abotraba distillation plant $0.008.

4.4.2.2.3. Fuel costs

Fuel is the largest overhead in terms of total production costs of water. The price of fuel against product water is directly influenced by fuel costs and likewise with product. Low productivity incurs high-steam consumption causing high-fuel consumption. Despite relatively constant prices of fuel in Libya, international prices can fluctuate, e.g. fuel oil ≈ $28/ton (Al-Hengari et al., 2015). Different types of fuel are used in MED-TVC units such as natural gas (propane gas), light and heavy fuel. The price of the former has been set at $0.007/$m^3$ by GDCOL. However, the total estimated annual expenditure of light and heavy fuel during 2010 was $620,122.1 and $2,823,712.07 respectively with annual water production of 12,277,009 m^3. Therefore, the calculated cost of light and heavy fuel per m^3 of desalted water for Abotraba distillation plant is $0.005 and $0.23 respectively.

4.4.2.2.4. Power consumption cost

Consumption of power is dictated by plant capacity and distillation method. MED units consume more power than MED-TVC plants because they have high power consumption demands. Overall, power overheads for heavy industrial operations in Libya are calculated at $0.52kWh (International Monetary Fund, 2013). Total annual expenditure in 2010 was estimated at $1,018,991.75 with annual total water production at 12,277,009 m^3 making the cost of power consumption (kWh) per m^3 of desalted water for Abotraba distillation plant to be $0.083.

4.4.2.2.5. Steam consumption costs

The evaporation procedure in MED-TVC units requires high-purity water for the purposes of generating steam. The annual total expenditure for water consumption in 2010 was $98,216.1 with total annual water production of 12,277,009 m^3 making the calculated cost of generating the steam per m^3 of desalted water at $0.008.

4.4.2.2.6. Maintenance costs

Maintenance costs are calculated according to provision of spare parts, man-hours (skilled and unskilled) according to level of skills, plant size and capacity, age and location as an annual fixed cost. The annual expenditure in 2010 for maintenance was $85,939.1 with a total annual water production of 12,277,009 m^3 making the calculated cost of maintenance per m^3 of desalted water to be $0.007.

4.4.2.2.7. Cleaning costs

There are daily cleaning costs alongside periodic cleaning procedures, which are authorised and carried out by local contracted firms to include the control room, internal roads, seawater pump station, chlorination unit and the management areas. At regular intervals, specialised cleaning is performed by the maintenance department at Abotraba distillation plant who focus on the cleaning of the seawater intake area, boiler and evaporation cells. The total annual expenditure in 2010 was estimated at $61,385.1 with the total annual water production 12,277,009 m^3 making the calculated cost of cleaning per m^3 of desalted water $0.005.

4.4.2.2.8. Cars and heavy machinery

At the beginning of 2010, the General Desalination Company of Libya supplied four cars for the management staff and two forklift vehicles for chemical and maintenance departments to the Abotraba Distillation Plant. The annual total expenditure was $159,601.1 with total water production of 12,277,009 m^3 making the calculated cost of cars and heavy machinery per m^3 of desalted water $ 0.013.

4.5. Results and discussion

Libya has witnessed an increase in population and growth rate. Censuses conducted in Libya have revealed that the overall population has increased significantly from 2.272 million in 1972 to 5.19 million in 2012. The population growth rate in the years 1982, 1992, 2002 and 2012 was equal to 3.82%, 1.07%, 1.63% and 1.85% respectively (**fig 4.7**). Such population growth usually increases demand for water in all sectors to satisfy its needs and the present limited water resources will undoubtedly become depleted over time.

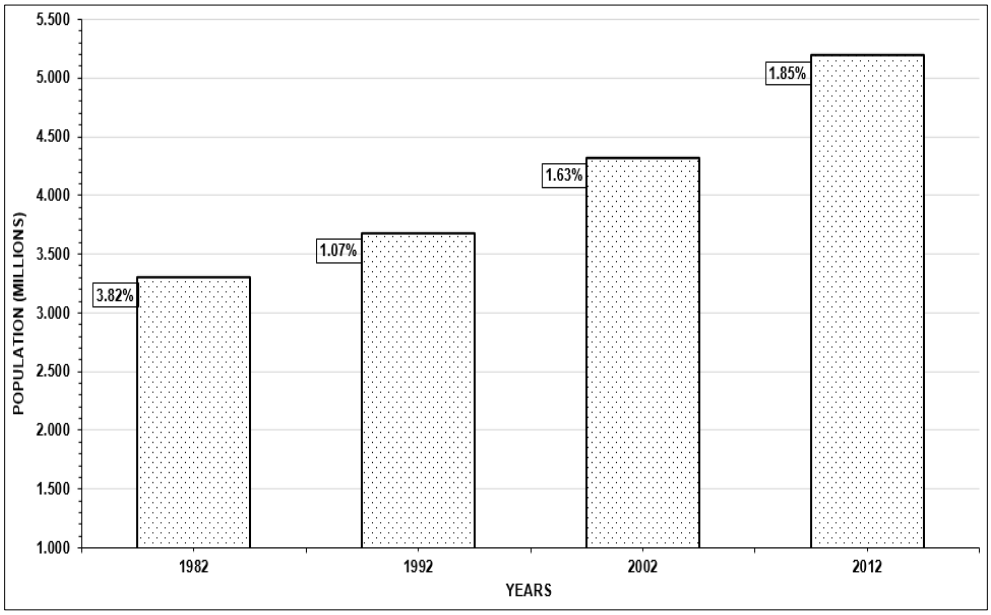


Figure 4. 7: Libyan population between 1982 and 2012 (Bureau of Statistics and Census Libya, 2013)

There are a wide range of policies pertaining to different aspects of water use, development and protection practised by different water authorities in the country. However, there is no actual defined policy, which makes clear distinction between all parties involved in the practice. This has caused confusion and lack of clear guidelines or line of management regarding water management. Currently, the water demand exceeds the conventional water resources capacities and there is a significant water shortage in some regions of the country; the highest annual water deficit is in Jabal Nafusah and Jifarah Plain region (fig 4.8) due to the population increases in this region following rapid increases in agricultural and industrial activities. In addition, some of the coastal aquifers have been depleted (Al Farrah et al., 2011) and some phases of the GMMR project have not yet been completed. Furthermore, there is a water deficit in the Middle Zone region because of an

increase in industrial sector activities and depletion of the council wells (General Water Authority, 2011). However, in Aljabal Alakhdar region, the water deficit is very low because it is supported by new desalination plants and dams (General Water Authority, 2011). In contrast, there is surplus water in Fezzan, Alkufrah and Assarir region because those regions are supplied by Great Man-Made River tanks; additionally, most studies have indicated that the lower ground layers are rich in fresh water in those regions (General Water Authority, 2011).

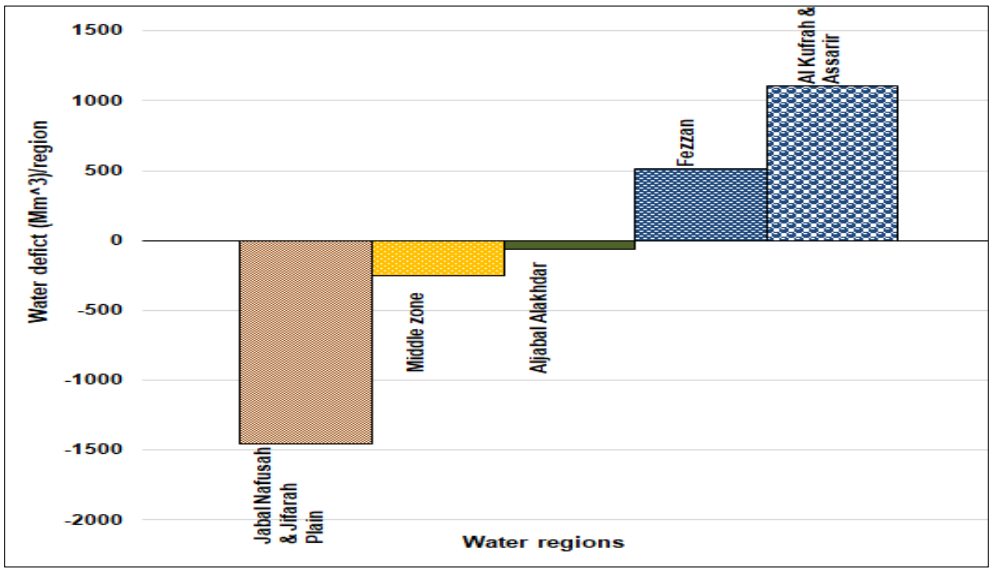


Figure 4. 8: Water Supply in Libyan water regions (El Asswad, 1995) (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

The Libyan government has implemented the GMMR project as an effort to tackle the issue of water shortage on the coastal belt, it is estimated that the total amount of water transferred by the GMMR project is about 6.18 million m^3/day. However, the project is not yet completed and the amount of water transferred is less than the amount planned, which is about 4.5 million m^3/day. The water supplied by the Great Man-Made River is higher in the agricultural sector (**60%**) than in the industrial sector (**2%**) and the goal of this is to support the agricultural sector in achieving agricultural self-sufficiency. Additionally, the amount of water allocated for the domestic use is around 38%, while the desalination stations do not contribute to the supply of water for agricultural purposes. The amount of water allocated to the domestic sector is higher (76%) than in the industrial sector (**24%**) (**fig 4.9**).

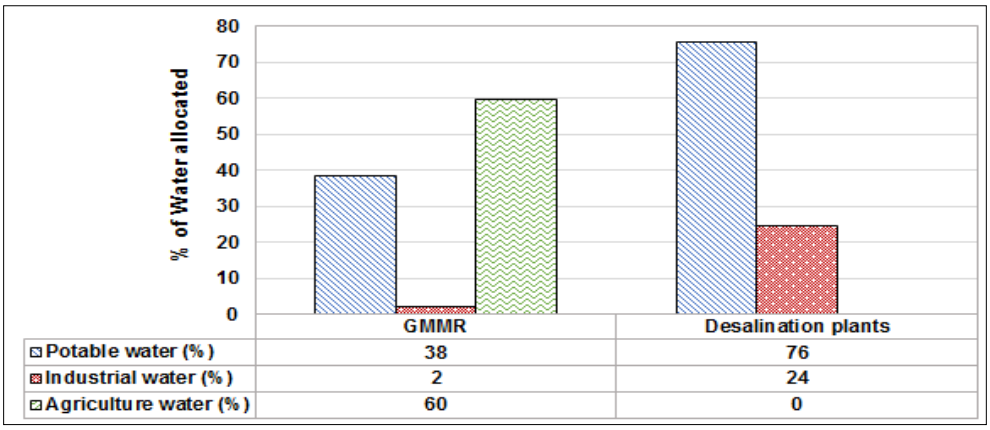


Figure 4. 9: Water allocated for various uses (Middle East business intelligence, 2010; General Desalination Company of Libya, 2013) (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

Recently, the total numbers of desalination stations operating in Libya was estimated to be more than 20 stations, with a total actual water production of 493,647 m^3/day (**Table 4.6**). Most desalination plants are located on the coastline belt of the country; hence, the total brine disposal from those plants is estimated to be 329,098 m^3/day, which is likely to pose a threat to the marine environment. The Libyan government is planning to increase the capacities of some coastal distillation plants which are authorised by General Water Desalination Company of Libya and General Electricity Company of Libya (**fig 4.10**).

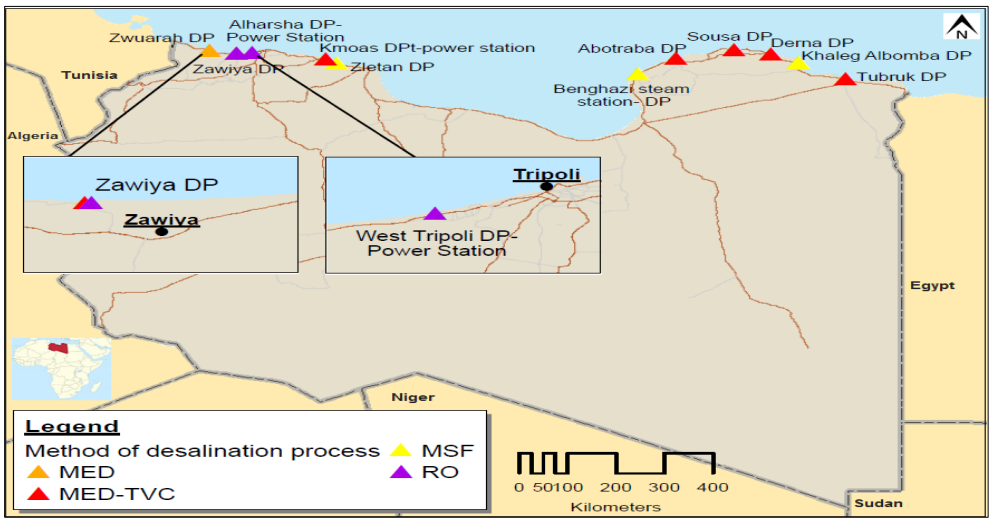


Figure 4. 10: Expanded capacities of distillation plants planned (ICRC, 2102) (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

With regard to the cost of a cubic metre produced from a thermal desalination plant, the total expenses include all the costs of water consumption during the desalination

process, fuel types, electrical energy consumption, chemical additives, fixed charges, labour, cleaning, cars and heavy machinery used in the plant in 2010**.**

From the data analysis (**fig 4.11**), its observed that the cost of a cubic metre of desalinated water by the multi-effect distillation with thermal compresses was about $0.43. In addition the cost of a cubic metre of light fuel was lower (0.005$) than the heavy fuel (0.23$), because the light fuel was used only in the start-up operation of the boilers.

In addition, the cost of power consumption was slightly higher (0.083$/m3) than the chemical additives (0.06$/m3) because the plant was designed with a hypochlorination unit which works to generate sodium hydroxide and sodium hypochlorite. The cost of the steam consumption used in the desalination process inside the plant was slightly higher (0.008$/m3) than the natural gas (0.007$/$m^3$) because natural gas is used in the start-up of the operation only.

Moreover, the cost of maintenance, labour, cleaning, cars and heavy machinery was equal to 0.007$/$m^3$,0.005$/m^3,0,0.013$/$m^3$ respectively. This study is consistent with previous studies, mentioned in the earlier chapter 2 (**section 2.6**) on the cost of a cubic metre of desalinated water, which depends on factors such as energy cost, desalination method, labour, maintenance cost… etc.

However, the previous studies estimate that the cost of desalinated water by thermal desalination technologies was slightly higher because the cost of desalinated water can be influenced by the design capacity of the plant and the exchange rate of the Libyan dinar versus the United States dollar. The cost of a cubic metre produced by thermal desalination plants in Libya was also examined with the capital cost and it was as low as $0.4 (Al-Hengari et al., 2015).

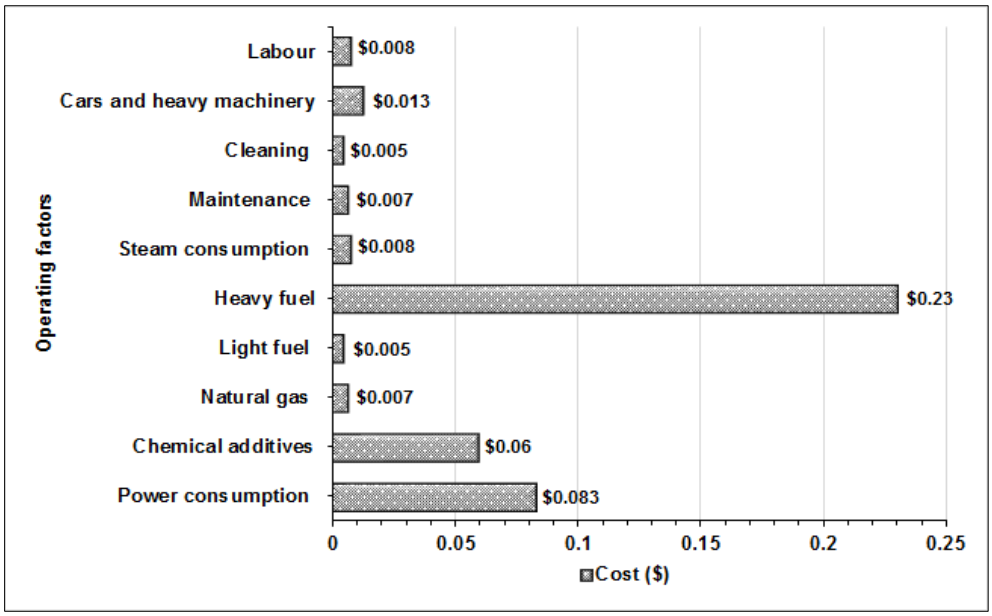


Figure 4. 11: Cost of a cubic metre of desalinated water by MED-TVC

The previous studies (Alghariani, 2007) revealed that the price of a cubic metre of water transferred by the GMMR for the first phase was 0.83 $, although the economic analysis performed during the conception of the GMMR project estimated that the price of a cubic metre transferred via the GMMR project to be approximately 0.25 $. Additionally, the water transferred during the two main phases is about 4.5 million m^3/day while the rest of the phases are still under construction. Hence, it is generally thought that this figure, which was calculated for the first stage of the GMMR project, will gradually increase during the remaining phases. Based on the above literature review and the results, it is important to explain that one of the major environmental concerns in Libya is the depletion of artesian aquifers water by the Great Man Made River as a result of overuse in the agricultural sector that may be causing a reduction in local groundwater wells, this will ultimately affect salinity and seawater penetration into the coastal aquifers. Another factor that contributes to environmental contamination is the use of pesticides for large-scale farming operatives which are supplied by the Great Man Made River.

4.6. Summary

Overall, it can be concluded that water resources in Libya are inadequate and seriously threatened by increased consumption by all sectors in response to an ever-

increasing population. The water management sector has a responsibility to safeguard the supply and provision of water in a holistic manner that ensures coordination from all stakeholders. This requires a seamless provision that involves all organisations involved in this vital service. There is a clear need for the Libyan government to take stock and establish clear policies that can be adopted by all those involved in the sustainable use of the nations's water resources.

According to the results and literature review regarding the best desalination technology in Libya, it is obvious that thermal desalination, such as MED, is the best option due to low cost, efficacy and reliability.

The next chapter will investigate the impact of thermal desalination plants on the Libyan coastline, which is the preferred location for future development and expansion.

Chapter Five: Environmental Impact of Brine Disposed from Distillation Plants on the Libyan Coastline

5.1. Introduction

The critical shortage of water in many Mediterranean countries, has led to environmental issues relating to sea water desalination plants, which had not been of prior concern, specifically, the results of the by-products discharge involved in the production of freshwater (Gacia et al., 2007; Einav and Lokiec, 2003). Moreover, there is still scant information about the impact of desalination effluent on the marine ecosystem (Safrai and Zask, 2008). This primarily comes to attention while dealing with the largest reverse osmosis (RO) operated desalination plants e.g. in (Moreno et al., 2014 and Torquemada et al., 2005). In Europe, 92% of all new installations apply membrane technology and most of them employ the seawater reverse osmosis technique (SWRO) (Trancki et al., 2012) being more efficient, both financially and operationally in terms of cost, space and energy usage (Pagès et al., 2010). Alternatively, multi-effect distillation techniques (MED) and multi-effect distillation techniques with thermal vapour compression (MED-TVC) are some of the most common techniques that provide a considerable quantity of potable and industrial water. These types of thermal desalination plants are preferred due to a number of advantages over other thermal desalination methods such as multi stage flash distillation technique (MSF). The following are some of the advantages: low operation costs, simple operating and maintenance procedures, high thermal efficiency, high heat transfer coefficient (Mazini, et al., 2014; Andrianne and Alardin, 2002), lower energy consumption and higher performance ratio. More recently, multi stage flash distillation technique (MSF) has been used (Al-Shayji, 1998) and seawater desalination plants are therefore often placed in close proximity to power plants to supply them with industrial water for steam to generate power (Trancki et al., 2012).

The most favoured brine disposal method is ocean brine disposal because of its efficiency and economic advantage over other methods (Torquemada et al., 2005; Ahmed et al., 2001). This option was generally acceptable for economic reasons but the vulnerability of the marine ecosystem towards changes in physico-chemical factors is making this method unsustainable, requiring more modern methods for

brine disposal (Einva and Lokiec, 2003). Therefore, economic reasons should not be the only factor to be considered when considering brine disposal techniques in order to safeguard the sustainability of the desalination process. Moreover, the ecological viability of desalination technologies needs to be assessed by four components which are environmental, economic, social and technological (Gude, 2016) reflecting a holistic approach to the sustainability of desalination technologies (Afgan et al., 1999). Indeed, desalination technologies of seawater offer a range of human health, socio-economic, and environmental benefits by providing a seemingly unlimited, constant supply of high quality water without impairing natural fresh water ecosystems (Lattemann and Höpner, 2008). However, there have been concerns about the environmental effects of high salinity (69,000psu), high thermal energy (at 11^0C temperature higher that the ambient seawater) and chemical additives on the marine ecosystem due to the release of brine by distillation plants (Pagès et al., 2010; Darwish et al., 2013).

Marine environments that receive the brine are typically subject to chemical and physical changes that can subsequently impact benthic communities. These alterations include deterioration in the quality of the seawater and sediment owing to harmful chemical components, which include heavy metals, antiscaling, antifouling, antifoaming and anticorrosion additive substances. In the same way, changes in physico-chemical characteristics of the seawater salinity, temperature, pH and dissolved oxygen might affect a considerable number of marine species (Naser, 2013; Lattemann and Höpner, 2002; Sadhwania et al., 2005; Torquemada et al., 2005).

One of these marine species is seagrass meadows which have become an area of concern as they are widespread across global coastal ecosystems (Moreno et al., 2014). The recent growth of desalination plants has altered the salinity levels in the Mediterranean Sea which vary between 36-40 (Latteman, 2010). This in turn has an adverse impact on benthic organisms (Yolanda and Luis, 2006), so the growth and development of seagrasses will subsequently be affected by osmotic stress resulting in compromised photosynthesis, reproduction and synthesis of new solutes (Moreno et al., 2014; Torquemada et al., 2005).

According to previous studies, *Posidonia oceanic*, a genus of seawater grass, is particularly sensitive to salinity of 38 psu causing growth reduction, 45 psu causing mortality, and 50 psu causing 100% mortality (Latorre, 2005; Torquemada and Lizaso, 2005). Furthermore, according to Ruiz and Romero (2001) it was found to have lower tolerance to other environmental factors such as reduction of light or high sedimentation rates (Manzanera et al., 1998). Consequently, this species is known as a stenobiotic seagrass making it very vulnerable to increased salinity levels of effluent from desalination plants (Hartog, 1970). Another type of seagrass known as *Cymodocea nodosa* also exists in marine environments subjected to a range of salinity levels ranging from 17-41 psu and according to experimental study it was found, with salinity levels below 17 psu and above 50 psu, causing sustained considerable mortality, and 56 psu causing 100% mortality (Sandoval et al., 2012;Yolanda and Luis, 2006). While different species displayed varying reactions for example it was observed that in areas of salinity up to a level of 50 psu, the size and survival rate of fish was reduced (Ahmed and Anwar, 2012; Parry, 1960).

In addition to salinity levels, other environmental factors contributed to the growth and diversity of seagrass such as temperature, dissolved oxygen and pH, also affecting the distribution and growth of several seagrass species (Torquemada et al., 2005; Hillman et al., 1995). Although desalination continues to be a growing industry in Libya, little has been done to study the environmental implications (Elfallah and Bosrgob, 2005).

Temperature is a key factor in the health and survival of many organisms, brine discharge has a relatively high temperature and low pH (Torquemada et al., 2005). Even a minimal increase to temperature (such as 1 ^{0}C) above ambient water over an extended period of time can alter species' metabolism and composition in an area and even result in death (Marsh et al., 1986; Hiscock et al., 2004). Some marine organisms can temporarily adapt to minor changes in temperature, but not for any length of time. For other marine life, long-term temperature change can be fatal (Lattemann and Höpner, 2008). For this reason, the co-location can reduce the impact on the marine environment through mixing the power plant's cooling water with the effluent from distillation plants, so the combined emissions will dilute the concentration of the brine and can speed up the dissolution of thermal and saline

effluent in the sea (Ahmad and Baddour, 2014). As temperature and salinity levels rise, the solubility of gases declines resulting in reduced levels of dissolved oxygen in seawater (Tonner, 2006) which limits respiration in marine organisms (Ahmed and Anwar, 2012). In turn, photosynthesis of marine angiosperms is compromised because the main ion hydrogen (pH) influences the concentration and formation of available carbonates (Torquemada et al., 2005; Beer and Waisel 1979). The three types of seagrasses were examined by Invers et al., 1997 to determine the effect of pH on their photosynthesis, namely *Posidonia oceanica*, *Cymodocea nodosa*, and *Zostera noltii* under controlled lab conditions. The former two displayed reduced levels of photosynthetic rates with an increase in pH and showed a significant reduction in net primary productivity (NPP) rates at pH 8.8. Conversely, *Z. noltii* showed high photosynthetic rates up to pH 8.8 but a significant reduction in primary productivity (NPP) rates at only pH 9.0.

Desalination processes require considerable heat and electrical energy which ultimately produces CO_2 emissions. Fossil fuels provide the source of this energy for thermal and RO processes (Tzen, 2014). In Mediterranean countries such as Libya, most of the distillation or power plants are designed to burn crude oil, gas-oil or heavy fuel oil (Enka, 2013). The products of combustion most commonly released by fossil fuel are ash particles, carbon dioxide (CO_2), carbon monoxide (CO), water vapour, Sulphur dioxide (SO_2), and nitrogen oxides (NOx) (European Union, 2012). Dissolved inorganic carbon (DIC) exists in seawater in three major forms: bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}), and aqueous carbon dioxide (CO_2 (aq)), which here also includes carbonic acid (H_2CO_3). At a pH of 8.2, ~88% of the carbon is in the form of HCO_3^-, 11% in the form of CO_3^{2-}, and only ~0.5% of the carbon is in the form of dissolved CO_2. When CO_2 dissolves in seawater, H_2CO_3 is formed. Most of the H_2CO_3 quickly dissociates into a hydrogen ion (H^+) and HCO_3^-. A hydrogen ion can then react with a CO_3^2 ion to form bicarbonate. Therefore, the net effect of adding CO_2 to seawater is to increase the concentrations of H_2CO_3, HCO_3^-, and H^+, and decrease the concentration of CO_3^{-2} and lower pH (Fabry et al., 2008), which are potential factors in global warming and oceanic acidification. Previous work indicates that the oceanic uptake of anthropogenic CO_2 and the concomitant changes in seawater chemistry have adverse consequences for many calcifying organisms, and may result in changes to

biodiversity, trophic interactions, and other ecosystem processes (Royal Society, 2005).

Research on the impact of the desalination plants on the marine environment has been recently carried out on some regional seas with high desalination activity, particularly in the Mediterranean Sea e.g. in Spain (Moreno et al., 2014; Torquemada and Lizaso, 2005); the Arabian Gulf e.g. in Saudi Arabia, Bahrain, Qatar and the United Arab Emirates (Hashim and Hajjaj, 2005; Naser, 2014; Uddin, 2014); the Red Sea e.g. in Egypt (Mabrook,1994; Qdais, 2008; Rasul and Stewart, 2015) or the southern coast of Australia in the upper Spencer Gulf (Dupavillon and Gillanders 2009), However, the majority of this work was conducted with mesocosms experiments under controlled conditions whereas little has been done in situ to test the tolerance of marine species to a real brine discharge (Ruíz et al., 2009; Gacia et al., 2007). Robets et al., (2012) reviewed about 62 scientific articles on brine discharge in marine water and found that 44% are mainly general discussions or opinions and lacked adequate quantitative data with regard to the impact on the marine environment. Although plans are in place to install further desalination plants on the Libyan coastline (Elhassadi, 2013), no scientific research has been carried out to study the environmental implications and the potential threat to marine ecosystems, therefore this chapter aims to determine the physico-chemical effects of brine influx from thermal desalination plants on the receiving water and, further to this, to evaluate their impact on the marine ecosystems at the Zwuarah and West Tripoli distillation plants (ZWDP &WTRIS) on the Libyan coastline, where the marine environment is considered to be highly exposed to brine discharges.

5.2. Methods and Materials

5.2.1. Study Sites

This study was conducted in May 2013 on the Libyan coastline around the Zwuarah and the West Tripoli distillation plants (ZWDP & WTRIS) (**fig 5.1**), which were built by a French company called SIDEM. ZWDP was first commissioned in 2006, located in the north-western side of the city of Tripoli (N 32.88333°, E 12.166667°). Freshwater in this plant was obtained by the application of thermal energy to the

seawater feed in multi effect stages without thermal vapour compression (MED) creating a distillate of fresh water while the brine stream is returned to the sea. ZWDP produces around 40,000 m^3day^{-1} of effluent to the marine environment of which 26,666.7 m^3day^{-1} is brine water. WTRIS was built in 1999 located west of the city of Tripoli (N 32.825822° E 12.972039°). The plant operates on a dual purposes basis to feed the power station with industrial water and produce freshwater, while concentrated brine steam is injected into the sea. WTRIS produces around 10,000 $m^3.day^{-1}$ with a total brine discarded 6,666.7 $m^3.day^{-1}$.

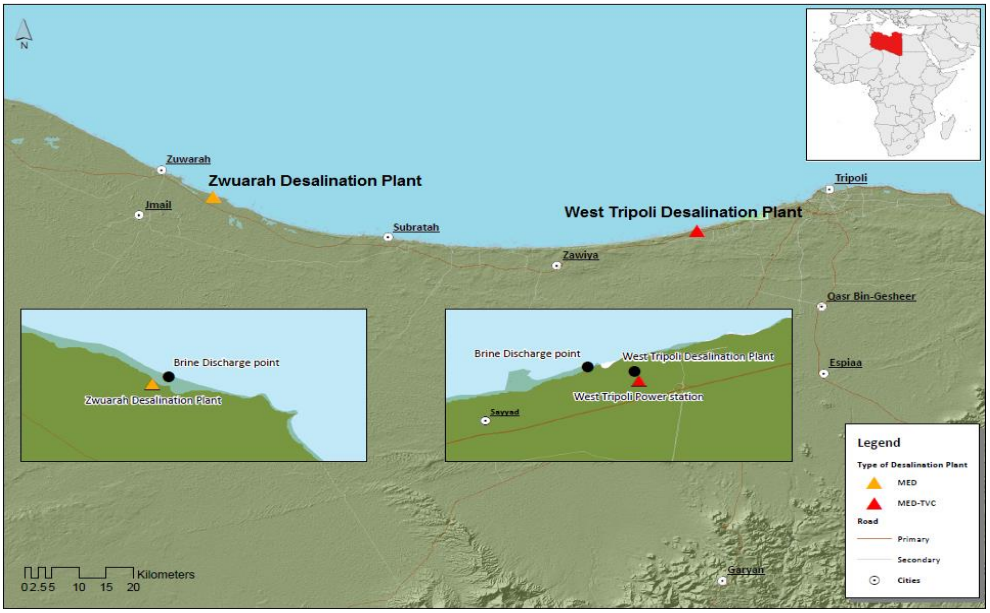


Figure 5. 1: Location of the ZWDP and WTRIS on the Libyan Coastline

5.2.2. Seawater Samples

Thirty eight stations (nineteen per site) were orientated in the direction where the brine was discarded at ZWDP and WTRIS (**fig 5.2**). At the two selected study sites, seawater samples were collected in a Nansen bottle of seven litres from each of the stations at both sites with different depths using GPS Map 420s to assess physiochemical parameters of seawater. Seawater samples bottles (300 & 500 ml) were rinsed with seawater from the Niskin bottle and then filled with sample seawater through a hose in order to reduce the contact with the atmosphere and it was numbered according to the station number. 1 mL of the WK1 manganese and 1 mL of WK2 alkaline-iodide reagents were added to each sample using a pre-calibrated pipette head and then intubated in a plastic bucket. Care is taken to ensure

that the samples are exposed to as little air as possible in order to keep the concentration of dissolved oxygen constant for each sample.

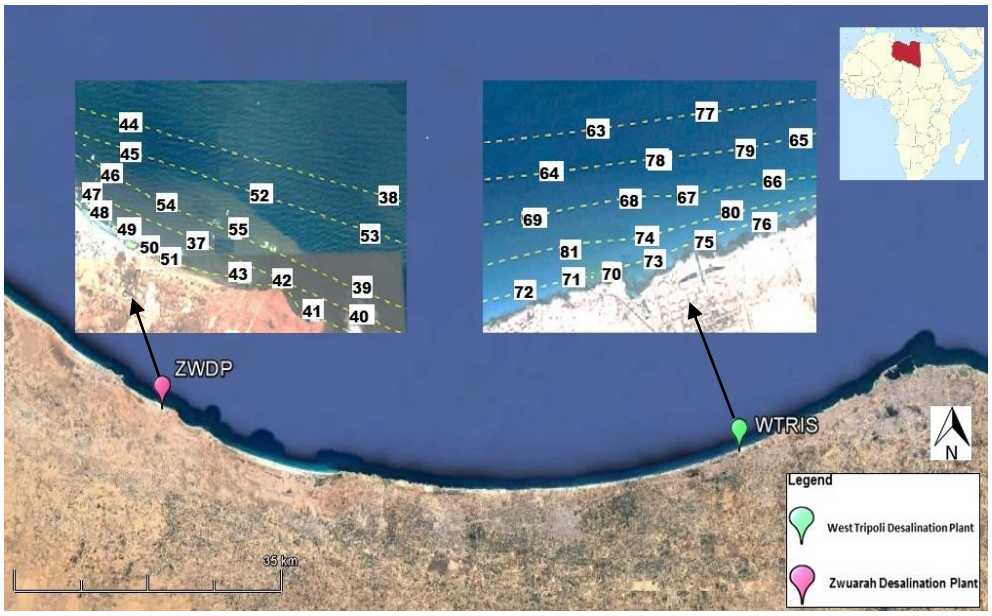


Figure 5. 2: Sampling location at ZWDP and WTRIS on the Libyan Coastline: (Google earth, 2016)

Physico-chemical parameters for the two selected sites, including salinity (psu), conductivity (µS/cm), dissolved Oxygen (mgl^{-1}), pH and total dissolved solids (mgl^{-1}), bottom and surface temperature (C^0) were measured immediately at the time the seawater was sampled by using a YSI 556 MPS handheld Multiparameter instrument (YSI Ltd, Hampshire, UK). total alkalinity (mgl^{-1}), bicarbonate (mgl^{-1}), total hardness (mgl^{-1}), calcium and magnesium hardness (mgl^{-1}), chloride (mgl^{-1}), nitrate (mgl^{-1}), sulphate (mgl^{-1}), phosphorus (mgl^{-1}), sodium (mgl^{-1}), potassium (mgl^{-1}), calcium (mgl^{-1}), magnesium (mgl^{-1}), nitrate (mgl^{-1}) and iron (mgl^{-1}) were analysed in the lab at ZWDP (**Table 5.1 and Table 5.2**). Additionally, brine samples disposed from each plant (ZWDP & WTRIS) were analysed (**Table 5.3**) according to Hach methods, 2013 for water, wastewater and seawater to determine physico-chemical parameters (**see appendix 5)**.

Table 5. 1: Measurement of Physico-chemical Parameters for Zwuarah Desalination Plant near to the outfall

Physico-chemical Parameters							Test Method	YSI 556 multiprobe	YSI 556 multiprobe	Hach Method 8203	Hach Method 8203	Hach Method 8213	Hach Method 8203	Hach Method 8203	Hach Method 8207	Lange LCK 339	Lange LCK 353	Lange LCK349	Flame photometer	Flame photometer	ASTM D1126-1	ASTM D1126-1	Hach Method 8008	YSI 556 multiprobe
GPS point	Station	Latitude: N	Longitude:E	Depth (m)	Temperature on the sea surface (^{0}C)	Temperature in the sea bottom (^{0}C)	Test Parameter	pH	Salinity (PSU)	Total alkalinity CaCO3 (mg/l)	Bicarbonate HCO3-(mg/l)	Total Hardness as CaCO3 (mg/l)	Calcium Hardness as CaCO3 (mg/l)	Magnesium Hardness as CaCO3 (mg/l)	Chloride (mg/l)	Nitrate (mg/l)	Sulfate (mg/l)	Phosphorus total (mg/l)	Sodium (mg/l)	Potassium (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Iron (mg/l)	oxygen (mg/l)
37	St 1	32.892200	12.182430	9.90	26.00	24.00	**Result**	8.35	43	120.1080	120.1080	10,600	900	9,700	23,581	0.10	2,805	0.10	17,440	490.00	360.360	2,355	0.07	7.86
38	St 2	32.895220	12.204580	8.40	25.00	24.00	**Result**	8.37	37	80.0720	80.0720	6,846	200	6,646	20,702	0.00	1,500	0.01	14,800	420.00	80.080	1,614	0.00	8.39
39	St 3	32.887240	12.201320	8.30	28.50	27.00	**Result**	8.36	35	88.0792	88.0792	7,090	290	6,800	19,374	0.10	1,500	0.01	15,210	430.00	116.116	1,651	0.02	5.67
40	St 4	32.885510	12.200550	1.90	29.60	27.00	**Result**	8.40	35	96.0864	96.0864	7,500	300	7,200	19,374	0.10	1,500	0.01	15,390	430.00	120.120	1,748	0.02	5.37
41	St 5	32.885300	12.195690	2.80	29.00	27.00	**Result**	8.46	36	96.0864	96.0864	10,300	300	7,700	19,651	0.10	2,000	0.01	15,420	430.00	120.120	1,870	0.02	5.7
42	St 6	32.888560	12.192220	4.80	26.00	25.00	**Result**	7.85	45	110.0468	110.0468	9,636	700	8,936	24,633	0.00	2,537	0.03	17,100	470.00	280.280	2,170	0.06	7.84
43	St 7	32.889007	12.187804	9.80	26.00	24.00	**Result**	8.04	45	116.0000	116.0000	10,031	831	9,200	24,702	0.10	2,671	0.04	17,170	480.00	287.080	2,234	0.07	7.69
44	St 8	32.902530	12.175740	2.50	26.70	24.00	**Result**	8.03	37	88.0792	88.0792	6,000	200	5,800	20,204	0.00	1,000	0.00	11,050	407.70	80.080	1,408	0.00	8.3
45	St 9	32.900362	12.174861	4.20	25.40	27.00	**Result**	7.95	36	104.0936	104.0936	9,120	565	8,555	19,927	0.10	2,000	0.02	16,430	450.00	203.600	2,077	0.04	7.96
46	St 10	32.898550	12.173006	3.60	28.10	29.10	**Result**	8.22	38	107.0700	107.0700	9,398	698	8,700	20,758	0.10	2,000	0.03	16,850	459.14	245.340	2,112	0.05	6.15
47	St 11	32.896554	12.171383	0.50	27.00	27.50	**Result**	8.02	40	108.5585	108.5585	9,500	700	8,800	21,865	0.10	2,500	0.03	16,890	469.43	280.280	2,137	0.06	7.14
48	St 12	32.895202	12.171271	0.60	28.00	28.90	**Result**	7.76	40	107.8100	107.8100	9,446	700	8,746	21,865	0.10	2,000	0.03	16,850	464.28	280.000	2,123	0.05	6.17
49	St 13	32.892919	12.174963	0.40	26.00	23.00	**Result**	8.08	37	104.0936	104.0936	9,332	632	8,700	20,204	0.10	2,000	0.03	16,675	460.00	224.470	2,112	0.04	7.49
50	St 14	32.891360	12.177020	0.40	37.00	35.50	**Result**	8.37	47	128.1152	128.1152	15,571	1,361	14,210	25,629	1.15	4,148	0.18	18,550	570.00	454.040	3,450	0.70	5.13
51	St 15	32.890755	12.179172	0.60	30.00	29.00	**Result**	8.12	45	120.1080	120.1080	14,900	1,100	13,800	25,075	0.10	3,074	0.11	17,900	490.00	440.440	3,351	0.07	5.18
52	St 16	32.896058	12.189978	6.80	28.00	25.00	**Result**	8.24	38	104.0936	104.0936	8,400	300	8,100	20,758	0.10	2,000	0.02	15,810	450.00	120.120	1,967	0.03	6.89
53	St 17	32.892424	12.202064	8.50	25.50	26.00	**Result**	8.18	37	104.0900	104.0900	8,200	300	7,900	20,647	0.10	2,000	0.01	15,738	448.85	120.120	1,918	0.02	7.96
54	St 18	32.895530	12.179240	5.50	26.00	27.00	**Result**	8.21	38	104.0936	104.0936	8,573	400	8,173	20,758	0.10	2,000	0.02	16,400	450.00	160.160	1,984	0.04	7.46
55	St 19	32.892700	12.187170	4.80	27.00	25.00	**Result**	8.19	38	104.0936	104.0936	8,400	300	8,100	21,256	0.10	2,000	0.02	16,206	450.00	120.120	1,967	0.04	6.98

Table 5. 2: Measurement of Physico-chemical Parameters for West Tripoli Desalination Plant near to the outfall

Physico-chemical Parameters							Test Method	YSI 556 multiprobe	YSI 556 multiprobe	Hach Method 8203	Hach Method 8203	Hach Method 8213	Hach Method 8203	Hach Method 8203	Hach Method 8207	Lange LCK 339	Lange LCK 353	Lange LCK349	Flame photometer	Flame photometer	ASTM D1126-1	ASTM D1126-1	Hach Method 8008	YSI 556 multiprobe
GPS point	Station	Latitude: N	Longitude:E	Depth (m)	Temperature on the sea surface (°C)	Temperature in the sea bottom (°C)	Test Parameter	pH	Salinity (PSU)	Total alkalinity CaCO3 (mg/l)	Bicarbonate HCO3-(mg/l)	Total Hardness as CaCO3 (mg/l)	Calcium Hardness as CaCO3 (mg/l)	Magnesium Hardness as CaCO3 (mg/l)	Chloride (mg/l)	Nitrate (mg/l)	Sulfate (mg/l)	Phosphorus total (mg/l)	Sodium (mg/l)	Potassium (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Iron (mg/l)	oxygen (mg/l)
63	St 1	32.834690	12.964960	22.00	24.00	22.00	**Result**	7.91	36	41	41	6,500	200	6,300	21,035	0.10	1,500	0.00	15,415	435	80	1,530	0.01	8.48
64	St 2	32.832150	12.962390	19.30	25.00	23.00	**Result**	8.00	36	45	45	6,819	269	6,550	22,073	0.10	2,000	0.00	15,725	450	108	1,590	0.02	8.00
65	St 3	32.834623	12.979451	17.60	24.00	22.00	**Result**	8.20	36	44	44	6,650	250	6,400	21,334	0.10	2,000	0.00	15,518	440	100	1,554	0.01	8.30
66	St 4	32.832140	12.977600	10.00	26.00	24.00	**Result**	8.10	35	47	47	6,850	275	6,575	23,027	0.10	2,000	0.01	15,980	450	110	1,596	0.02	7.96
67	St 5	32.830880	12.971510	4.50	26.00	22.00	**Result**	7.85	37	54	54	7,300	300	7,000	22,986	0.10	2,500	0.03	16,550	480	120	1,700	0.03	7.86
68	St 6	32.830880	12.967900	3.80	26.50	24.00	**Result**	8.10	43	50	50	6,900	300	6,600	22,142	0.10	2,000	0.01	16,190	470	120	1,602	0.02	7.94
69	St 7	32.829670	12.961240	11.80	26.30	24.00	**Result**	8.30	37	52	52	7,000	300	6,700	22,634	0.10	2,000	0.01	16,270	470	120	1,627	0.02	7.90
70	St 8	32.827290	12.967090	0.50	37.00	35.00	**Result**	8.20	55	172	172	10,161	1,361	8,800	24,850	0.20	2,843	0.15	17,000	510	545	2,137	0.13	7.06
71	St 9	32.826820	12.965150	0.50	38.00	36.50	**Result**	8.13	43	368	368	11,200	2,000	9,200	24,868	0.70	4,433	0.16	17,020	560	801	2,234	0.00	6.17
72	St 10	32.826051	12.961663	0.60	31.00	29.00	**Result**	8.34	42	82	82	8,700	700	8,000	24,079	0.10	2,586	0.05	16,740	490	280	1,942	0.03	7.43
73	St 11	32.827919	12.969882	0.50	27.00	25.00	**Result**	8.40	39	136	136	9,900	1,100	8,800	24,788	0.20	2,672	0.13	16,890	491	440	2,137	0.07	7.14
74	St 12	32.828930	12.969240	2.20	26.00	24.00	**Result**	7.86	39	86	86	9,200	900	8,300	24,721	0.20	2,629	0.08	16,870	490	360	2,015	0.04	7.31
75	St 13	32.828874	12.972887	0.50	25.00	23.00	**Result**	8.40	39	84	84	8,800	700	8,100	24,671	0.10	2,607	0.06	16,830	490	280	1,967	0.04	7.37
76	St 14	32.829930	12.976570	0.50	24.00	22.00	**Result**	8.00	37	52	52	7,286	300	6,986	22,813	0.10	2,490	0.03	16,550	480	120	1,696	0.03	7.88
77	St 15	32.835910	12.972850	18.00	22.00	21.00	**Result**	8.36	36	30	30	6,200	200	6,000	20,691	0.10	1,500	0.00	14,900	430	80	1,457	0.01	8.76
78	St 16	32.833140	12.969500	12.00	23.00	21.00	**Result**	8.47	37	40	40	5,000	200	4,800	20,617	0.10	1,500	0.01	11,680	410	80	1,165	0.00	8.96
79	St 17	32.833960	12.975690	8.50	23.00	21.00	**Result**	7.85	36	44	44	6,763	263	6,500	22,031	0.10	2,000	0.00	15,312	440	105	1,578	0.01	8.11
80	St 18	32.830322	12.974870	1.00	25.00	23.00	**Result**	8.20	36	62	62	7,700	500	7,200	23,119	0.10	2,500	0.04	16,570	490	200	1,748	0.03	7.76
81	St 19	32.828360	12.964400	3.50	28.00	26.00	**Result**	8.40	36	80	80	8,200	500	7,700	23,535	0.10	2,500	0.05	16,660	490	200	1,870	0.03	7.74

Table 5. 3: Measurement of Physico-chemical Parameters for Zwuarah and West Tripoli Desalination Plants from Evaporators

Test parameter	Test Method	Result-ZWDP	Result-WTRIS
pH	HQ40D metre test pro.	8.5	8.07
Salinity (PSU)	HQ40D metre test pro.	52,000-56,000	51,994 - 57,000
Total Alkalinity as $CaCO_3$ (mg/l)	Hach Method 8203	132	128
Carbonate CO_3^{--}(mg/l)	Hach Method 8203	0	0
Bicarbonate HCO_3^-(mg/l)	Hach Method 8203	132	128
Total Hardness as $CaCO_3$ (mg/l)	Hach Method 8213	10,509.50	8,347.50
Calcium Hardness as $CaCO_3$ (mg/l)	Hach Method 8203	1641.5	1361.22
Magnesium Hardness as $CaCO_3$ (mg/l)	Hach Method 8203	8,867.10	6,986.30
Chloride Cl^-(mg/l)	Hach Method 8207	28,784	21,050
Nitrate NO_3^-(mg/l)	Lange LCK 339	1.25	0.7
Sulphate SO_4^{--} (mg/l)	Lange LCK 353	8,530	4,433
Phosphorus total PO_4^{---}	Lange LCK349	0.174	0.158
Sodium Na+ (mg/l)	Flame photometer	12,870	11,680
Potassium k+ (mg/l)	Flame photometer	561.1	491.2
Calcium (mg/l)	ASTM D1126-1	657.3	545
Magnesium (mg/l)	ASTM D1126-1	2,153.15	1,696.28
Iron (mg/l)	Hach Method 8008	0.08	0.02
Temperature (^{0}C)	Hach Method HQ 40d	41-43	38-42.5
O_2 (mg/l)	Hach Method HQ 40d	4.3	3.9

5.2.3. Seabed Sediment Samples

Thirty eight seabed sediment samples were collected from each of the stations from the seafloor at both sites using a Van Veen Grab and a PVC pipe with a length of 40 cm and a diameter of 10 cm with two stoppers at each end which is also used for collecting the sea sediments for stations. Each sample was stored in a plastic bag and labelled according to the station number so that each sample could be identified (depths 0.4 to 9.9 m, ZWDP; 0.5 to 22 m, WTRIS; Garmin GPS Map 420s). All sediment samples were stored in a refrigerator at < -18 C° in the laboratory of the Marine Biology Research Centre of Tajura, Libya, where the sediments experiments were conducted. Organic content of the sediments was assessed (**Table 5.4)** and grain size was analysed **(Table 5.5 & 5.6)** according to Folk 1974 method for defining sediment type and degree of sediment kurtosis (KG), Skewness (SKI) and Standard Deviation (δI).

Table 5. 4: Organic content level (%) of the sediments for Zwuarah and West Tripoli Desalination Plants

Organic content level (%) for ZWDP					Organic content level (%) for WTRIS				
GPS.P	Station	Latitude	Longitude	Organic content level (%)	GPS.P	Station	Latitude	Longitude	Organic content level (%)
37	St 1	32.89220	12.18243	4.50	63	St 1	32.83469	12.96496	8.47
38	St 2	32.89522	12.20458	7.90	64	St 2	32.83215	12.96239	7.60
39	St 3	32.88724	12.20132	5.60	65	St 3	32.83462	12.97945	8.43
40	St 4	32.88551	12.20055	5.60	66	St 4	32.83214	12.97760	6.06
41	St 5	32.88530	12.19569	5.10	67	St 5	32.83088	12.97151	5.22
42	St 6	32.88856	12.19222	5.10	68	St 6	32.83088	12.96790	5.30
43	St 7	32.88901	12.18780	4.80	69	St 7	32.82967	12.96124	4.97
44	St 8	32.90253	12.17574	7.30	70	St 8	32.82729	12.96709	4.97
45	St 9	32.90036	12.17486	5.90	71	St 9	32.82682	12.96515	1.04
46	St 10	32.89855	12.17301	6.50	72	St 10	32.82605	12.96166	1.08
47	St 11	32.89655	12.17138	4.90	73	St 11	32.82792	12.96988	2.16
48	St 12	32.89520	12.17127	4.90	74	St 12	32.82893	12.96924	6.42
49	St 13	32.89292	12.17496	3.40	75	St 13	32.82887	12.97289	2.57
50	St 14	32.89136	12.17702	2.80	76	St 14	32.82993	12.97657	3.49
51	St 15	32.89076	12.17917	4.10	77	St 15	32.83591	12.97285	9.70
52	St 16	32.89606	12.18998	5.80	78	St 16	32.83314	12.96950	7.90
53	St 17	32.89242	12.20206	6.60	79	St 17	32.83396	12.97569	8.03
54	St 18	32.89553	12.17924	4.40	80	St 18	32.83032	12.97487	3.81
55	St 19	32.89270	12.18717	5.10	81	St 19	32.82836	12.96440	2.72

Table 5. 5: Classification used for defining sediment type and degree of sediment kurtosis (KG), Skewness (SKI) and Standard Deviation (δI) for ZWDP.

Sediment Analysis - Zwuarah Station						*Sediment classification*					*Graphic Kurtosis (KG)*						*Inclusive Graphic Skewness (SKI)*					*Inclusive Graphic Standard Deviation (δI)*						
GPS point	Station	Mean grain size (Mz)	Graphic Kurtosis (KG)	Inclusive Graphic Skewness (SKI)	Inclusive Graphic Standard Deviation (δI)	Coarse sand (0.5-1 mm) or (0.0-1Ø)	Medium sand (0.25-0.5 mm) or (1-2 Ø)	Fine sand (0.125-0.25 mm) or (2-3Ø)	Very fine sand (0.062-0.125 mm) or (3-4Ø)	Mud (less than 0.062 mm) or (more than 4Ø)	(0.41-0.67 Ø) Very platykurtic	(0.67-0.90 Ø) platykurtic	(0.90-1.11Ø) mesokurtic	(1.10-1.50 Ø) leptokurtic	(1.50-3.00 Ø) very leptokurtic	(3.00 Ø) extremely leptokurtic	(+1 to + 0.30) strongly positive skewed – Very negative phi valued, coarse	(+ 0.3 to + 0.10) positive skewed-Negative phi values	(+ 0.10 to - 0.1) Near symmetrical-Symmetrical	(- 0.10 to - 0.30) Negative skewed-positive phi values	(- 0.30 to - 1.00) strongly negative skewed-very positive phi values, fine	(0.00-0.35 Ø) very well sorted	(0.35-0.50 Ø) well sorted	(0.50-0.71 Ø) moderately well sorted	(0.71-1.00 Ø) moderately sorted	(1.00-2.00 Ø) poorly sorted	(2.00-4.00 Ø) very poorly sorted	(4.00 Ø) extremely poorly sorted
37	St 1	1.43	1.15	0.3	0.97		■							■				■								■			
38	St 2	2.46	0.69	-0.2	0.70			■				■									■				■				
39	St 3	3.03	0.88	-0.3	0.98				■			■									■					■			
40	St 4	3.13	1.07	0.0	0.42				■				■						■					■					
41	St 5	3.60	1.02	0.3	0.50				■				■					■						■					
42	St 6	2.93	0.76	0.1	0.42			■				■							■					■					
43	St 7	2.53	0.74	-0.4	0.96			■				■										■				■			
44	St 8	1.06	0.43	-0.1	0.49		■				■										■			■					
45	St 9	1.03	0.60	0.0	0.49		■				■									■				■					
46	St 10	2.26	1.39	-0.3	0.51			■						■							■				■				
47	St 11	2.26	1.39	-0.2	0.51			■						■							■				■				
48	St 12	2.03	0.94	-0.2	0.65			■					■								■				■				
49	St 13	2.26	1.99	-0.3	0.91			■							■							■				■			
50	St 14	1.50	0.99	0.2	1.40		■						■				■									■			
51	St 15	2.40	1.54	-0.1	0.52			■							■						■				■				
52	St 16	1.40	1.13	0.1	1.07		■							■			■								■				
53	St 17	1.19	0.75	-0.3	0.88		■					■										■				■			
54	St 18	1.50	0.79	0.4	1.19		■					■						■								■			
55	St 19	1.23	1.79	0.2	0.96		■									■	■									■			

Table 5. 6: Classification used for defining sediment type and degree of sediment kurtosis (KG), Skewness (SKI) and Standard Deviation (δI) for WTRIS.

Sediment Analysis - West TRI Plant						*Sediment classification*					*Graphic Kurtosis (KG)*						*Inclusive Graphic Skewness (SKI)*					*Inclusive Graphic Standard Deviation (δI)*						
GPS point	Station	Mean grain size (Mz)	Graphic Kurtosis (KG)	Inclusive Graphic Skewness (SKI)	Inclusive Graphic Standard Deviation (δI)	Coarse sand (0.5-1 mm) or (0.0-1Ø)	Medium sand (0.25-0.5 mm) or (1-2 Ø)	Fine sand (0.125-0.25) or (2-3 Ø)	Very fine sand (0.062-0.125) or (3-4 Ø)	Mud (less than 0.062) or (more than 4 Ø)	(0.41-0.67 Ø) Very platykurtic	(0.67-0.90 Ø) platykurtic	(0.90-1.11Ø) mesokurtic	(1.10-1.50 Ø) leptokurtic	(1.50-3.00 Ø) very leptokurtic	(3.00 Ø) extremely leptokurtic	(+1 to +0.30) strongly positive skewed – Very negative phi valued, coarse	(+0.3 to +0.10) positive skewed-Negative phi values	(+0.10 to -0.1) Near symmetrical-Symmetrical	(-0.10 to-0.30) Negative skewed-positive phi values	(-0.30 to -1.00) strongly negative skewed-very positive phi values, fine	(0.00-0.35 Ø) very well sorted	(0.35-0.50 Ø) well sorted	(0.50-0.71 Ø) moderately well sorted	(0.71-1.00 Ø) moderately sorted	(1.00-2.00 Ø) poorly sorted	(2.00-4.00 Ø) very poorly sorted	(4.00 Ø) extremely poorly sorted
63	St 1	2.10	0.89	-0.04	0.40			■				■							■					■					
64	St 2	2.42	2.34	-0.26	0.32			■							■					■			■						
65	St 3	2.49	2.73	0.15	0.29			■							■		■						■						
66	St 4	2.10	0.87	-0.34	0.53			■				■										■			■				
67	St 5	1.91	0.92	-0.07	0.69		■						■						■						■				
68	St 6	2.30	1.25	-0.50	0.43			■						■							■			■					
69	St 7	2.57	0.86	0.03	0.75			■				■							■						■				
70	St 8	2.30	1.39	-0.10	0.46			■						■					■					■					
71	St 9	0.70	2.54	0.11	0.37	■									■				■				■						
72	St 10	1.93	0.96	0.07	0.59		■						■						■						■				
73	St 11	2.76	1.26	0.28	0.52			■						■			■								■				
74	St 12	2.73	0.86	-0.14	0.89			■				■							■						■				
75	St 13	1.30	1.18	-0.04	0.89		■							■					■						■				
76	St 14	1.80	1.28	0.48	0.56		■							■								■			■				
77	St 15	2.13	1.39	0.23	1.00			■						■							■					■			
78	St 16	1.90	1.27	0.08	0.87		■							■				■								■			
79	St 17	1.93	0.85	0.16	0.83		■					■					■									■			
80	St 18	3.00	1.07	-0.07	0.77			■					■						■							■			
81	St 19	2.06	1.38	0.26	0.49			■						■			■							■					

5.2.4. Biological Sample Collection

Video footage was recorded by a scuba diver at both sites along transect lines (**fig 5.2**) close to the seafloor by using a Fuji finepix f500 exr camera with Fuji wp-fxf500 housing at different depths from 0.4 to 9.9 m at ZWDP and from 0.5 to 22 m at WTRIS measured using Garmin GPS Map 420s. From each video 138 still images were randomly sampled and analysed (sixty-eight images for ZWDP and seventy for WSTRI images) using Image J Analysis software (Random Systematic Sampling) (Rasband, W.S., ImageJ, U.S. National Institutes of Health, Bethesda, MD http://imagej.nih.gov/ij/, 1997-2012) to determine percentage coverage for each species found in the photographs. The chosen size for each photo taken was 20.00×20.00 cm and a 100 random dots grid (= 100%) was overlayed over each photo. The species underneath each dot in the photo was counted and identified.

5.3. Statistical Analysis

PRIMER® v 6 software (Plymouth Routines In Multivariate Ecological Research Version Six) was used (Clarke and Gorley 2006). Mean and ± Standard Error for community composition between the stations at each site (ZWDP & WTRIS) were analysed statistically. Differences in the community composition between the stations at each site were assessed using multivariate techniques based on the Bray-Curtis Similarity index ANOSIM (Clarke, 1993) which is a simple non-parametric permutation procedure applied to a similarity matrix underlying the ordination or classification. ANOSIM calculates an R values (Global test) that lies between 0 and 1 (Chapman and Underwood, 1999). The global R is similar to a regression analysis to measure how well the data modelling fits to the reality (Malcolm and Lancaster, 2013), with R values of 1 denoting complete difference existing between groups and zero denoting no difference is observed between groups. If R is approximately zero, then the null hypothesis is accepted and if R equals 1 then the null hypothesis is rejected. R value will usually fall between 0 and 1 indicating some degree of discrimination between sites and the statistical significance that was chosen for the test for two sites between those stations was set at $p<0.05$ and the average similarity, dissimilarity and abundance between stations were identified by using the SIMPER test (Clarke,1993) for each site, which looks at the role of individual species in contributing to the separation between two groups of samples and to

determine the main species contributing to the groups identified during the cluster analysis. Average Bray-Curtis dissimilarity was used between all pairs of sample and represented within this test. The nMDS plots were produced in terms of their species composition at the selected sites. The nMDS analysis plots a measure of similarity between the stations into multi-dimensional spaces so that the distance between objects corresponds closely to their input similarities. Simply stated, the closer two dots on the nMDS plot are the more similar the samples/stations. The stress value indicates how precisely the high dimensional relationships among the samples are represented, the lower the stress value, the less distortion occurs (Hargrave, 2005).

The physico-chemical and seabed data (organic content levels and grain size) data for the different stations at both sites were normalised and then characterised by the principal component analysis (PCA scores; Primer etc). PCA scoring is a standard parametric ordination technique that plots the distribution of physico-chemical parameters and seabed data at each station in usually two dimensions based on linear combinations of variables. It is particularly suited for the analysis of physico-chemical parameters and seabed sediments (organic content levels and grain size) data, further to summarise the statistical correlation between the physico-chemical parameters and seabed sediments (organic content levels and grain size) data with minimum loss of original information. Inspection of the correlation matrix revealed the presence of many coefficients of 0.3 or greater, in order to identify the important factor into each PCA (Pallant, 2010). Williams et al., 2010 stated that a factorability of 0.3 indicates that the factors account for approximately 30% relationship within the data. However, Hair et al., 1995 categorised these loadings using another rule of thumb as ± 0.30 = minimal, ± 0.40 = important, and ±.50=practically significant.

Thus, as data from PCA scores did not meet ration level, linear relativity and normal bivariate distribution, nonparametric spearman's rank correlation analysis was performed (Walls et al., 2013) using SPSS statistical software (IBM Corp. Released 2011. IBM SPSS Statistics for Windows, Version 20.0. Armonk, NY: IBM Corp) (**see appendix 5**). This was applied in order to determine the relationship between the physico-chemical, seabed sediments (organic content levels and grain size) parameters and the benthic community. If there are no repeated data values, a

perfect Spearman correlation of +1 or -1 occurs when each of the variables is a perfect monotone function of the other (Tabachnick and Fidell, 2013; Field, 2013). Level of significance for all tests was 5%.

5.4. Results

5.4.1. Differences between Stations in Community Composition at ZWDP

Eight different species were found at ZWDP which included the seagrasses *Posidonia oceanica* and *Cymodocea nodosa*, unknown sea algae, the brown alga *Taonia atomaria*, the red alga *Laurencia pinnatifida*, the brown alga *Padina pavonica*, the brown alga *Sargassum vulgare* and fish *Spicara flexuosa*, *Diplodus annularis* and *Diplodus vulgaris*. Furthermore, non-living substrata such as sand and sea rocks were also found (**fig 5.3**). There was a significant difference in the community composition between the 10 stations (Global R: 0.6332, $p<0.001$; **fig. 5.4**).

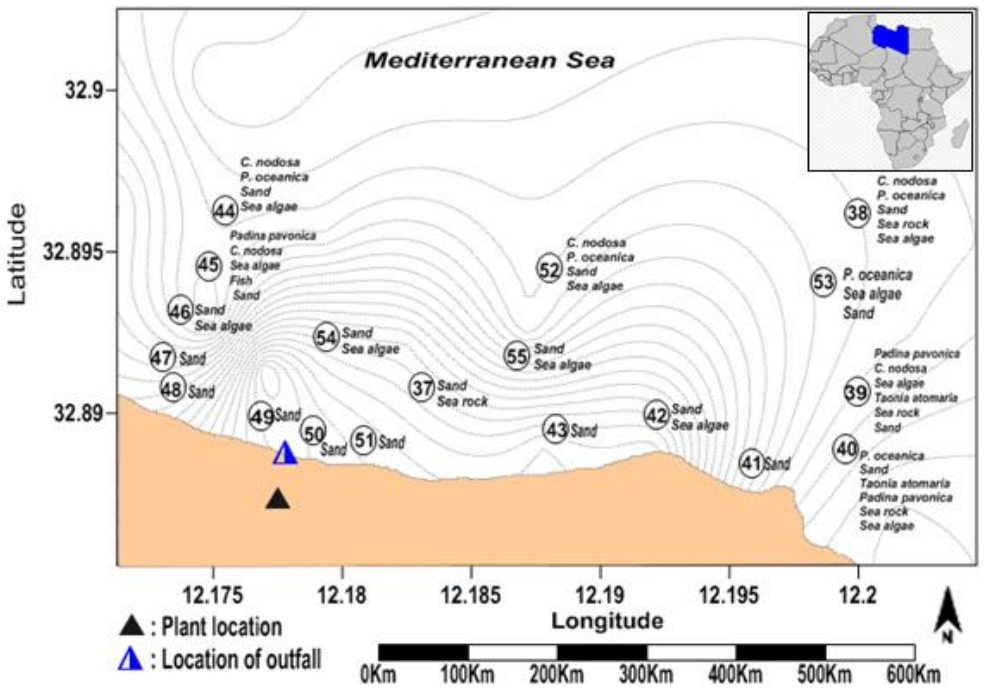


Figure 5. 3: Community Composition at each Station for ZWDP (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

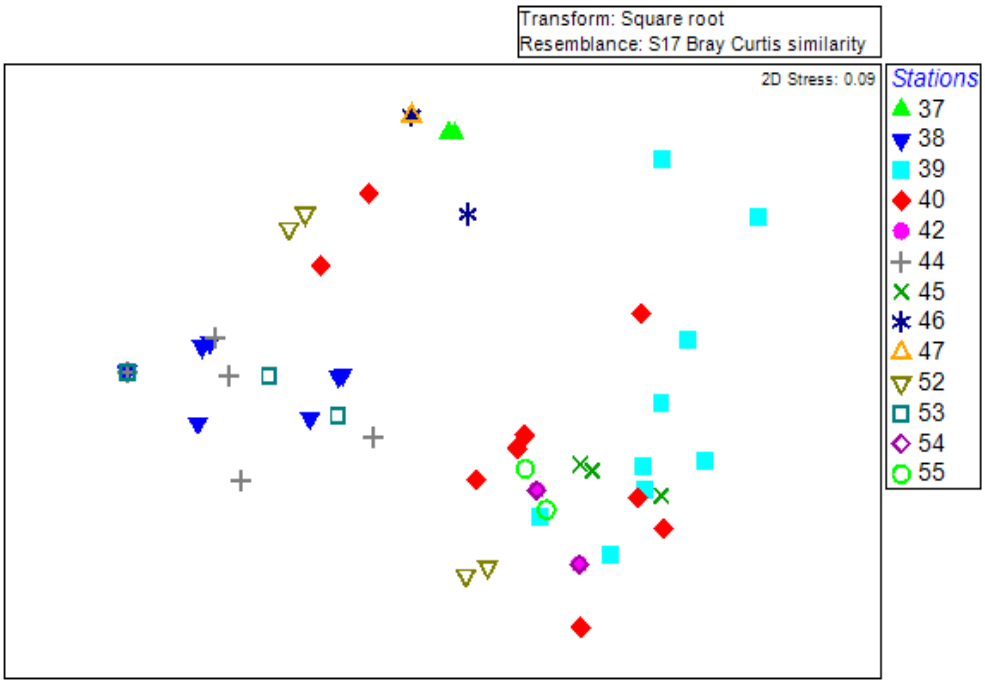


Figure 5. 4: Two-dimensional ordination plots from multidimensional scaling analysis of Bray-Curtis similarity index (2D stress: 0.09; 5 replicates per station).

There was a significant difference in the community composition between stations 37, 38, 39, 44 and 53 (38: Global R: 1, p< 0.001; average dissimilarity 92.02%; 39: Global R: 0.912, p< 0.001; average dissimilarity 97.31%; 44: Global R: 1, p< 0.001; average dissimilarity 94.75%; 53: Global R: 1, p<0.001; average dissimilarity 97.10%). *P. oceanica* contributed 44.61% to the average dissimilarity between station 37 and 38, 42.74% to the average dissimilarity between stations 37 and 44 and 97.10% to the average dissimilarity between stations 37 and 53. Average percentage cover of *P. oceanica* was higher at station 38 (82.11%±42.96%) than at station 37 where it was zero. Similarly, average percentage cover of *P. oceanica* was higher at station 44 (81%±41.72%) than at station 37 where it was zero. Likewise, average percentage cover of *P. oceanica* was a higher at station 53 (93.70%±48.07%) than at station 37 where it was zero. Unknown sea algae contributed 27.12% to the average dissimilarity between stations 37 and 39 with a higher average percentage cover at station 39 (52.78%±33.30%) than at station 37 where it was zero. While, *Padina pavonica* contributed 9.93% to the average dissimilarity between stations 39 and 37 with a higher average percentage cover at station 39 (19.28%±15.56%) than at station 37 where it was zero. There was a significant difference in the community composition between stations 38, 39 and 40 (39: Global R: 0.911, p= <0.001; average dissimilarity 94.34%; 40: Global R:

0.709, p=<0.001; average dissimilarity 86.88%). *P. oceanica* contributed 43.50% to the average dissimilarity between stations 38 and 39 and 44.51% to the average dissimilarity between stations 38 and 40. Average percentage cover of *P. oceanica* was higher at station 38 (82.11%±42.96%) than at station 39 where it was zero. Similarly, average percentage cover of *P. oceanica* was higher at station 38 (82.11%±42.96%) than at station 40 (4.78%±8.44%). Unknown sea algae contributed 26.43% to the average dissimilarity between station 38 and 39 and 26.85% to the average dissimilarity between stations 38 and 40. Average percentage cover of unknown sea algae was lower at station 38 (5.22%±15.87%) than at station 39 (52.78%±33.30%). While, average percentage cover of unknown sea algae was higher at station 40 (49.56%±30.95%) than at station 38 (5.22%±15.87%). The other important species at these stations was *Padina pavonica* which contributed 10.24% to the average dissimilarity with a higher average percentage cover at station 39 (19.28%±15.56%) than at station 38 where it was zero. Similarly, *Sargassum vulgare* contributed 4.63% to the average dissimilarity with a higher average percentage cover at station 39 (8.78%±23.20%) than at station 38 where it was zero (**fig 5.5**). Moreover, *Laurencia pinnatifida* contributed 7.48% to the average dissimilarity with a higher average percentage cover at station 40 (13%±13.24%) than at station 38 where it was zero (**fig 5.6**). There was a significant difference in the community composition between stations 39, 44 and 53 (44: Global R: 0.943, p=<0.001; average dissimilarity 96.21%; 53: Global R: 0.961, p=<0.001; average dissimilarity 97.19%). *P. oceanica* contributed 42.07% to the average dissimilarity between stations 44 and 39 and 48.18% to the average dissimilarity between stations 53 and 39. Average percentage cover of *P. oceanica* was higher at station 44 (81%±0%) than at station 39 where it was zero. Similarly, average percentage cover of *P. oceanica* was higher at station 53 (93.7%±48.06) than at station 39 where it was zero. Unknown sea algae contributed 26.72% to the average dissimilarity between stations and 39 and 44 and 26.19% to the average dissimilarity between stations 39 and 53. Average percentage cover of unknown sea algae was higher at station 39 (52.78%±4.38%) than at station 44 (4.38%±19.4%). Similarly, the average percentage cover of unknown sea algae was higher at station 39 (52.78%±33.3%) than at station 53 (3.4%±31.01%). In addition, *Padina pavonica* contributed 10.04% to the average dissimilarity between station 39 and 44 and 9.94% to the average dissimilarity between stations 39 and

53. Average percentage cover of *Padina pavonica* was higher at station 39 (19.28%±15.56%) than at station 44 where it was zero. Similarly, average percentage cover of *Padina pavonica* was higher at station 39 (19.28%±51.56%) than at station 53 where it was zero (**fig 5.7**). Moreover, *C. nodosa* contributed 4.88% to the average dissimilarity between stations 39 and 44 with a lower average percentage cover at station 39 (0.11%±0.29%) than at station 44 (9.38%±28.9%) (**fig 5.8**). There was a significant difference in the community composition between stations 40, 44 and 53 (44: Global R: 0.733, p=<0.001; average dissimilarity 89.42%; 53: Global R: 0.821, p=<0.001; average dissimilarity 91.39%). *P. oceanica* contributed 42.62% to the average dissimilarity between stations 40 and 44 and 48.65% to the average dissimilarity between stations 40 and 53. Average percentage cover of *P. oceanica* was lower at station 40 (4.78%±8.44%) than at station 44 (81%±41.72%). Similarly, average percentage cover of *P. oceanica* was lower at station 40 (4.78%±8.44%) than at station 53 (93.7%±48.06%). Unknown sea algae contributed 26.60% to the average dissimilarity between stations 40 and 44 and 26.20% to the average dissimilarity between stations 40 and 53. Average percentage cover of unknown sea algae was higher at station 40 (49.56%±30.95%) than at station 44 (4.38%±19.4%). Similarly, the average percentage cover of unknown sea algae was higher at station 40 (49.56%±30.95%) than at station 53 (3.4%±31.01%). In addition**,** *Laurencia pinnatifida* contributed 7.27% to the average dissimilarity between stations 40 and 44 and 7.11% to the average dissimilarity between stations 40 and 53. Average percentage cover of *Laurencia pinnatifida* was higher at station 40 (13%±13.24%) than at station 44 where it was zero (**fig 5.9**). Similarly, the average percentage cover of *Laurencia pinnatifida* was higher at station 40 (13%±13.24%) than at station 53 where it was zero (**fig 5.10**).

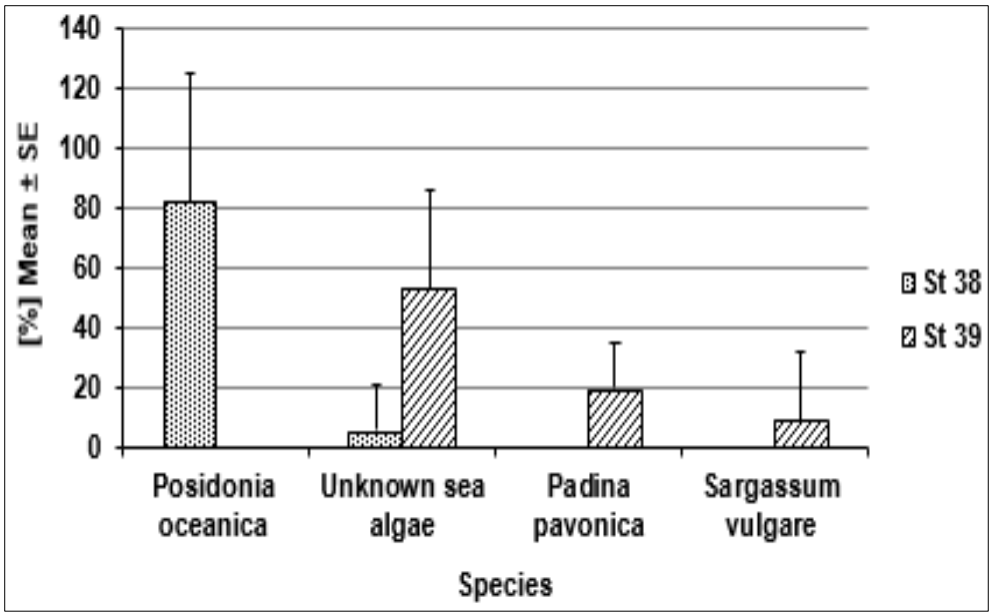


Figure 5. 5: Species coverage [%] Mean ± SE between station 38 and 39

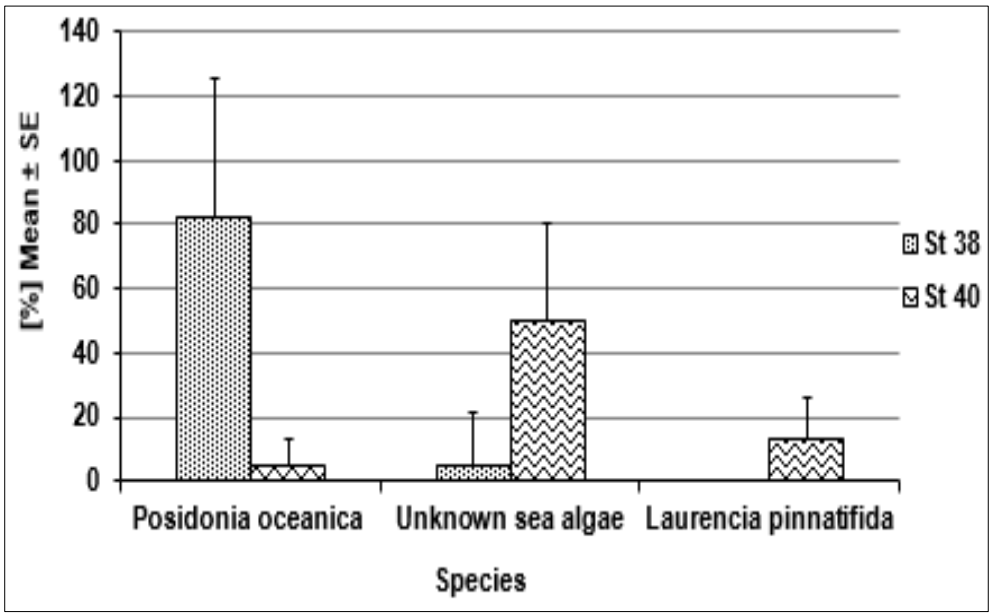


Figure 5. 6: Species coverage [%] Mean ± SE between station 38 and 40

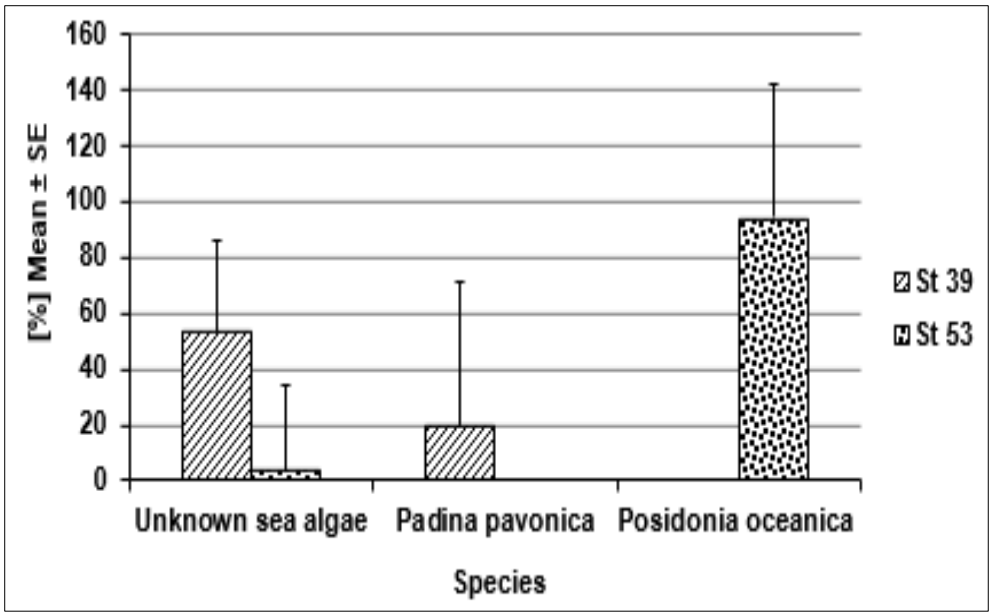


Figure 5. 7: Species coverage [%] Mean ± SE between station 39 and 53

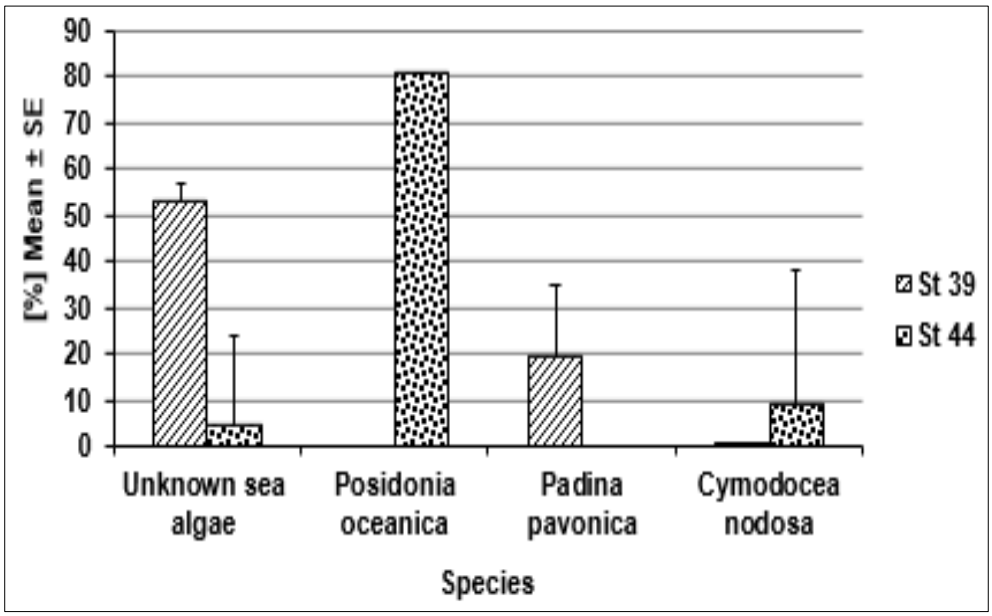


Figure 5. 8: Species coverage [%] Mean ± SE between station 39 and 44

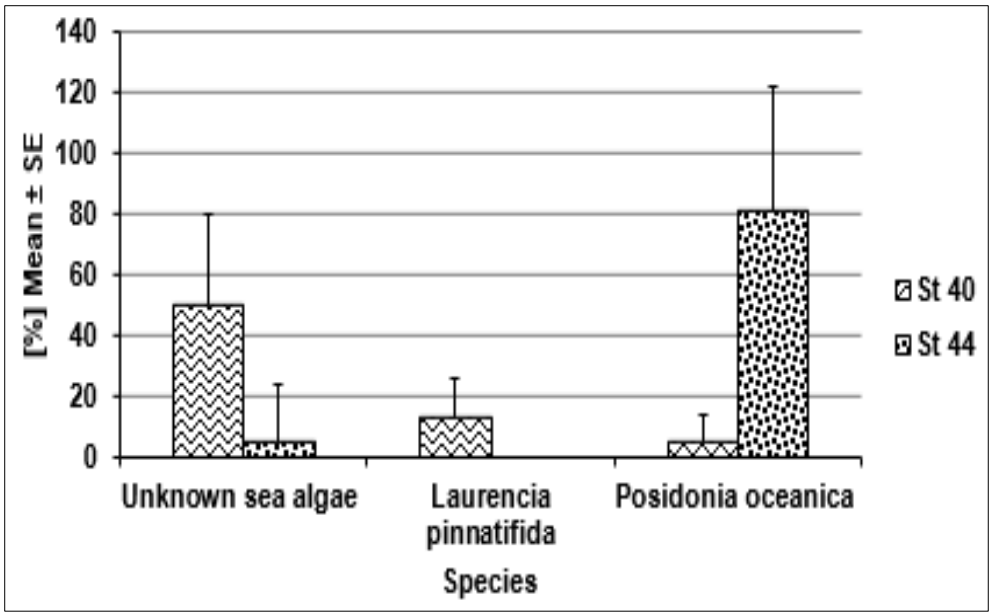


Figure 5. 9: Species coverage [%] Mean ± SE between station 40 and 44

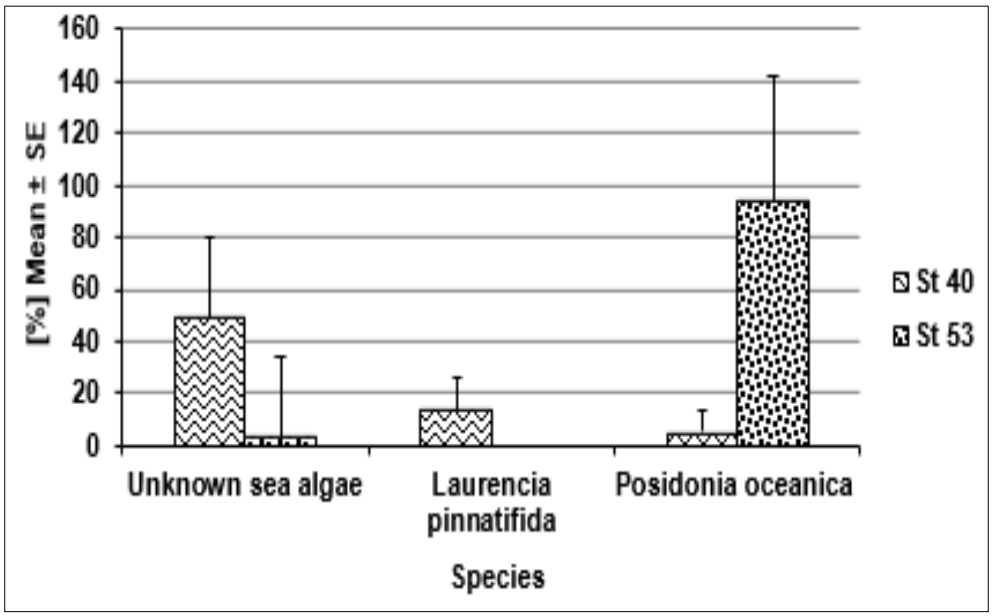


Figure 5. 10: Species coverage [%] Mean ± SE between station 40 and 53

5.4.2. Differences between Stations in Community Composition at WTRIS

Four species were found at WTRIS which included the seagrasses *Posidonia oceanica* and *Cymodocea nodosa*, fish *Xyrichtys novacula* and *Diplodus annularis* and a sea anemone species *Anemonia sulcate*, in addition to non-living substrata such as sand and sea rocks (**fig.11).** There was a significant difference in the

community composition between the 10 stations (Global R: 0.31, p<0.0001; **fig 5.12**).

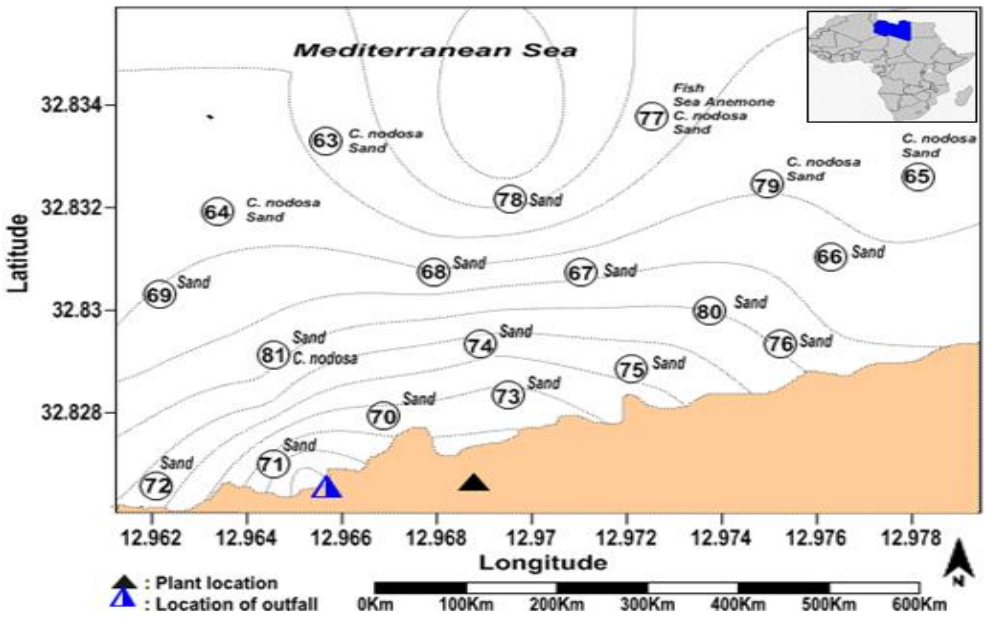


Figure 5. 11: Community Composition at each Station for WTRIS

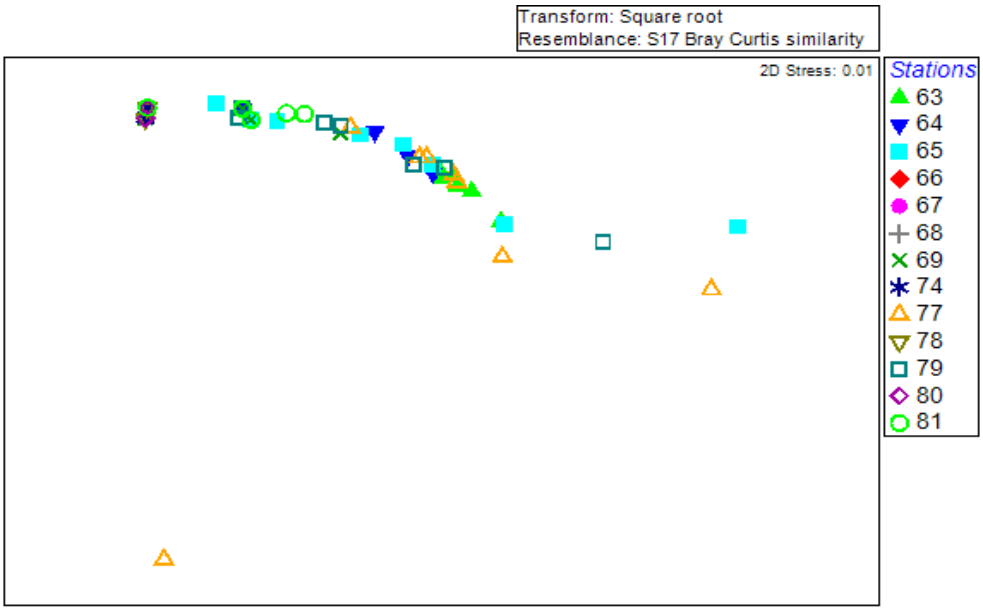


Figure 5. 12: Two-dimensional Ordination plots from multidimensional scaling analysis of bray-Curtis similarity index (2D stress: 0.01; 5 replicates per station) for WTRIS

There was a significant difference in the community composition between stations 63, 65, 77, 78 and 79 (65: Global R: 1, p= <0.001; average dissimilarity 42.67%; 77: Global R: 0.536, p= <0.001, average dissimilarity 30.88%; 78: Global R: 0.628, p= <0.001; average dissimilarity 47.50%; 79: Global R: 0.646, p= <0.001; average

dissimilarity 25.81%). *C. nodosa* contributed 50% to the average dissimilarity between stations 63 and 78, 50% to the average dissimilarity between stations 65 and 78, 40.13% to the average dissimilarity between station 77 and 78 and 50.69% to the average dissimilarity between station 78 and 79. Average percentage cover of *C. nodosa* was higher at station 63 (42.67%±50%) than at station 78 where it was zero. Similarly, average percentage cover of *C. nodosa* was higher at station 65 (30.88%±50%) than at station 78 where it was zero. Likewise, average percentage cover of *C. nodosa* was higher at station 77 (38.13%±33.87%) than at station 78 where it was zero. In addition, average percentage cover of *C. nodosa* was higher at station 79 (25.93%±50.02%) than at station 78 where it was zero.

5.4.3. Environmental parameters at ZWDP

At ZWDP, PCA analysis on physico-chemical parameters resulted in five components (**fig 5.13**) and the pattern is best explained in PC1 with 67.6% of the total variance, however, addition of PC2, PC3, PC4 and PC5 accounted for 81.4%, 88.2%, 92.4% and 94.9% of the total variance respectively.

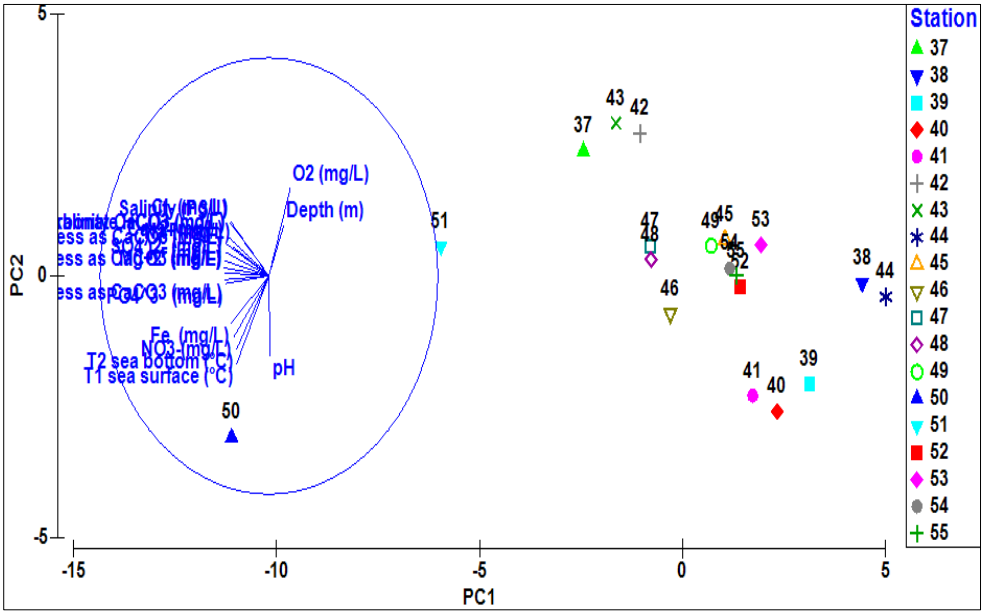


Figure 5. 13: Principal components analysis (PCA) ordination of physico-chemical parameters for ZWDP. (With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

The pattern between the stations in PC1 is best explained with Total hardness as $CaCO_3$ (mgl^{-1}) (-0.3), Ca^{+2} hardness as $CaCO_3$ (mgl^{-1}) (-0.3), Mg^{+2} hardness as

$CaCO_3$ (mgl^{-1}) (-0.3), SO_4^{-2} (mgl^{-1}) (0.3), PO_4^{-3} (mgl^{-1}) (-0.3), k^+ (mgl^{-1}) (-0.3), Ca^{+2} (mgl^{-1}) (-0.3) and Mg^{+2} (mgl^{-1}) (-0.3). In PC2 the pattern between the stations is best explained with sea surface temperature (°C) (0.4), sea bottom temperature (°C) (0.3), pH (0.3), NO^{3-} (mgl^{-1}) (0.3), O_2 (mgl^{-1}) (-0.4). In PC3 the pattern between the stations is best explained with Depth (m) (0.7) and pH (0.6). In PC4 the pattern between the stations is best explained with pH (-0.4), NO_3^- (mgl^{-1}) (0.4), Na^+ (mgl^{-1}) (-0.4), Fe (mgl^{-1}) (0.4) and Dissolved oxygen DO (mgl^{-1}) (0.5). In PC5 the pattern between the stations is best explained with salinity (psu) (0.4), Cl^- (mgl^{-1}) (0.4) and Na^+ (mgl^{-1}) (-0.5). Positive relationship between score of PC1 and seagrass percentage cover *Posidonia oceanic* was determined using Spearman rank correlation coefficient (r_s=0.673; p=0.002) at ZWDP.

Seabed sediment classification which is obtained from analysing the organic content levels and sieves for the mean grain size in (**Table 5.4 and 5.5 for ZWDP; section 5.2.3**) were categorised by the principal-component analysis (PCA) in order to determine the distribution of seabed sediment classification in area for ZWDP. At this site, PCA analysis on the seabed sediment resulted in two components representing the mean grain size and organic content levels at each station (**fig 5.14**) and the pattern is the best explained in PC1 with 53.7% of the total variance, however the PC2 accounted for 100% of the total variance.

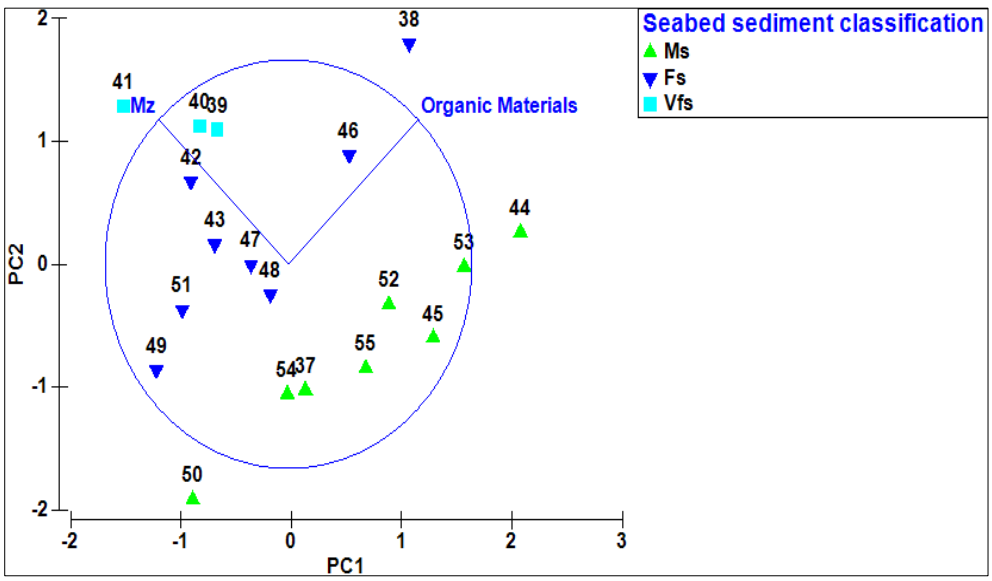


Figure 5. 14: Principal components analysis (PCA) ordination of sediment data for ZWDP: (sediment classifications: Ms= medium sand, Fs= fine sand, VFS=very fine sand).

The pattern between the stations in PC1 is best explained with organic material (g) (0.707) and mean grain size (Mz) (Ø) (-0.707). In the PC2, the pattern between the station is best explained with organic material (g) (-0.707) and mean grain size (Mz) (Ø) (0.707). The organic content levels which were reported in **(Table 5.4 for ZWDP; section 5.2.3**) for ZWDP (<10%) in all stations). Additionally, a positive relationship between organic content and seagrass (*P. oceanica*) was determined using Spearman rank correlation coefficient (r_s=0.573; p=0.001).

There was a significant positive correlation coefficient between organic content level in sediments and seagrass (*P. oceanica*) (r_s=0.573; p=0.01) and non-significant positive correlation coefficient between mean grain size and sea grass (*P. oceanica*) (r_s=0.359; p=0.132).

The statistical parameters of the grain size (Mz) have been a major parameter in delineating the influence of depositional processes. Generally, standard deviation and skewness are considered environmentally sensitive indicators, while the mean is a reflection of competence of the transport mechanism (Rabiu et al., 2011). The results obtained from the sieves analysis in **(Table 5.5; section 5.2.3 for ZWDP)** shows that the mean grain size (Mz), which is reflection of the overall size of the sediment, ranged from 1.03 Ø – 3.6 Ø (medium - fine - very fine sand) (**fig.5.15**), while the Graphic Kurtosis (KG) was between 0.66 Ø – 2.46 Ø (very platykurtic – platykurtic - mesokurtic - leptokurtic -very leptokurtic). Skweness (SKI) values ranged from -0.4 Ø to 0.4 Ø (strongly positive - positive - symmetrical - negative - strongly negative skewed) while the Inclusive Graphic Standard Deviation (δI) which is a measure of sorting varied from 0.4 Ø – 1.4 Ø (well-moderately well-moderately-poorly sorted). The classification of the sediments at ZWDP, show that the percentage cover of fine sand was higher than medium and very fine sand.

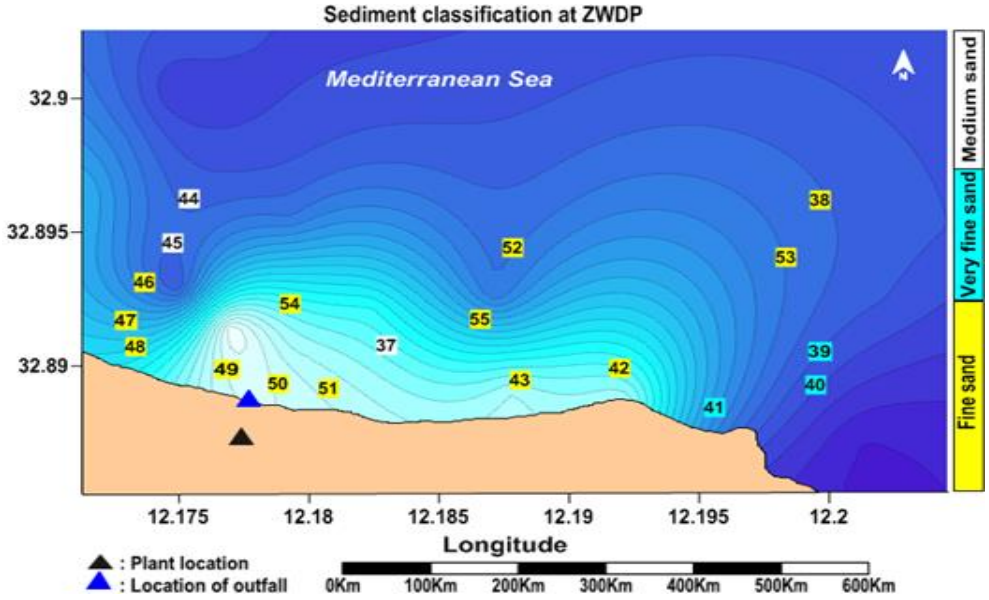
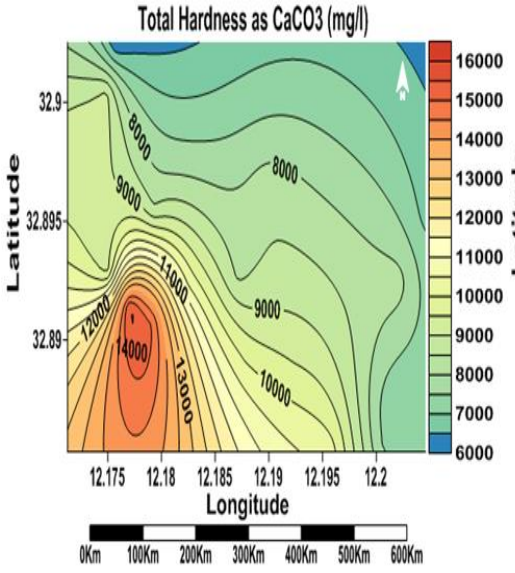


Figure 5. 15: The classification of the sediments at ZWDP

Differences in physico-chemical parameters in the seawater samples taken near the outfall of ZWDP indicated that all stations at this site have a wide variation in the level of total hardness as $CaCO_3$ mgl^{-1}, ranging from 6,000 to 15,571 mgl^{-1}. The minimum concentration of total hardness as $CaCO_3$ mgl^{-1} was observed at station 44 at 2.5 m depth and the maximum was observed at station 50 at 0.4 m depth (**fig 5.16**). The Ca^{+2} hardness as $CaCO_3$ mgl^{-1} in the seawater study area fluctuated between a minimum of 200 mgl^{-1} at station 38 at 8.4 m and a maximum of 1,361 mgl^{-1} at station 50 at 0.4 m depth (**fig 5.17**).



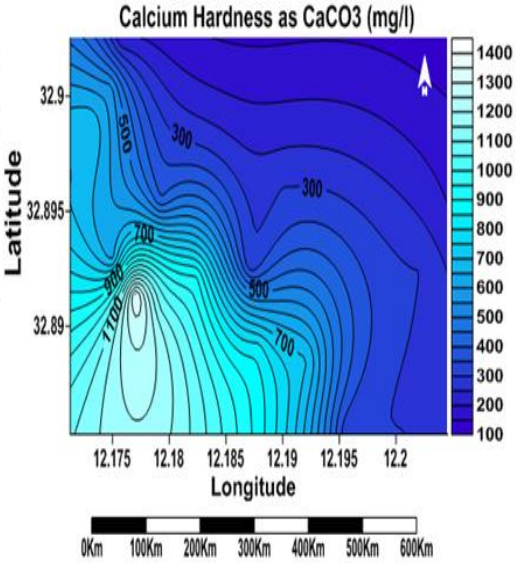
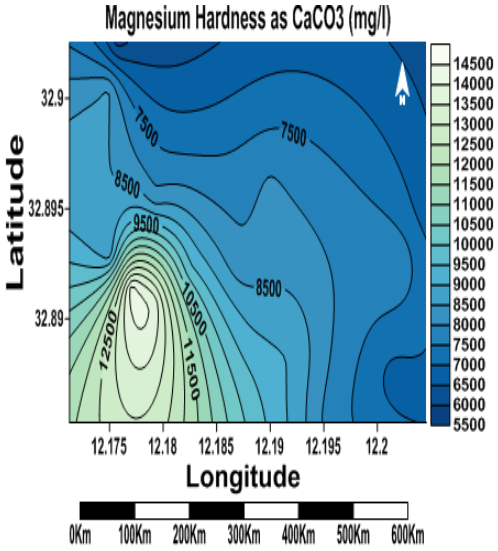


Figure 5. 16: Total Hardness (mgl^{-1}) at ZWDP

Figure 5. 17: Ca^{+2} Hardness (mgl^{-1}) at ZWDP

(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

The minimum concentration of Mg^{+2} hardness as $CaCO_3$ was 5,800 mgl^{-1} recorded at station 44 at 2.5 m depth, while maximum value was 14,210 mgl^{-1} detected at station 50 at 0.4 m depth (**fig 5.18**). All stations at ZWDP showed a wide variation in the concentration of calcium Ca^{+2} ions. The highest concentration of Ca^{+2} was at station 50 (Ca^{+2} =454 mgl^{-1}) at 0.4 m depth, while the lowest of Ca^{+2} was at station 38 and 44, with the same level (Ca^{+2}=80 mgl^{-1}) with 8.4 and 2.5 m depth respectively (**fig 5.19**).



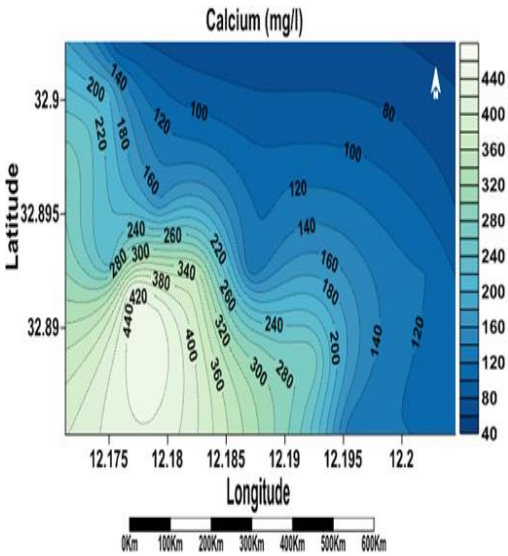
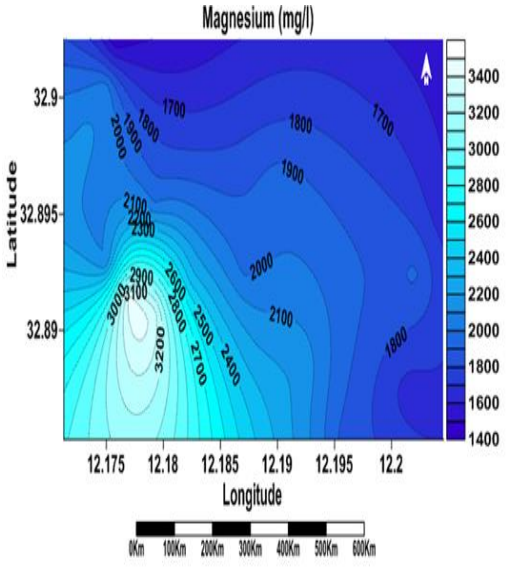


Figure 5. 18: Mg^{+2} Hardness (mgl^{-1}) at ZWDP **Figure 5. 19: Ca^{+2} (mgl^{-1}) at ZWDP**
(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

All stations had a wide variation in the concentration of magnesium ions Mg^{+2}. The highest concentration level was recorded at station 50 (Mg^{+2} =3,450 mgl^{-1}) with 0.4 m depth, while the lowest level of Mg^{+2} ion was reported at station 44 (Mg^{+2}=1,408 mgl^{-1}) with 2.5 m depth (**fig 5.20**). There was a wide variation in the concentration of Sulphate (SO_4^{-2}). The maximum concentration of SO_4^{-2} was observed at station 50 (SO_4^{-2} = 4,148 mgl^{-1}) at 0.4 m depth and the minimum concentration of SO_4^{-2} was recorded at station 44 (SO_4^{-2} =1,000 mgl^{-1}) at 2.5 m depth (**fig 5.21**). All stations indicated a narrow variation in the concentration of Potassium ions K^+ mgl^{-1}, varying from 408 to 570 mgl^{-1}. The lowest concentration of K^+ was observed at station 44 (K^+ =408 mgl^{-1}) at 2.5 depth, while the highest concentration of K^+ was found at station 50 (K^+ =570 mgl^{-1}) at 0.4 m depth (**fig 5.22**). All the stations at this site revealed a wide variation in the concentration of sodium ions (Na^+). High concentration of Na^+ was observed at station 50 at 0.4 m (Na^+ =18,550 mgl^{-1}), while

the lowest concentration was detected at station 44 (Na^{+} =11,050 mgl^{-1}) at 2.5 m depth (**fig 5.23**).



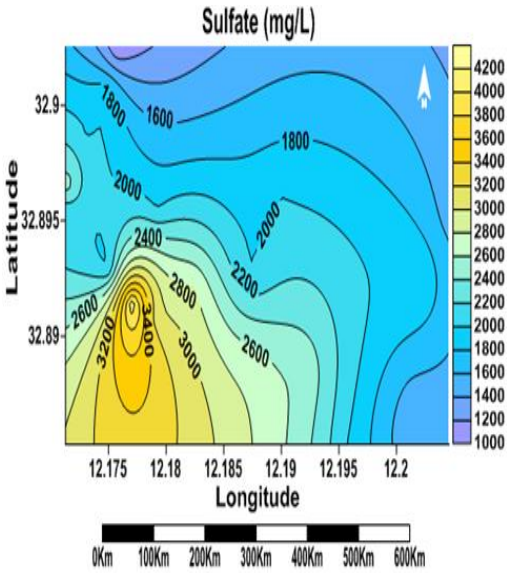
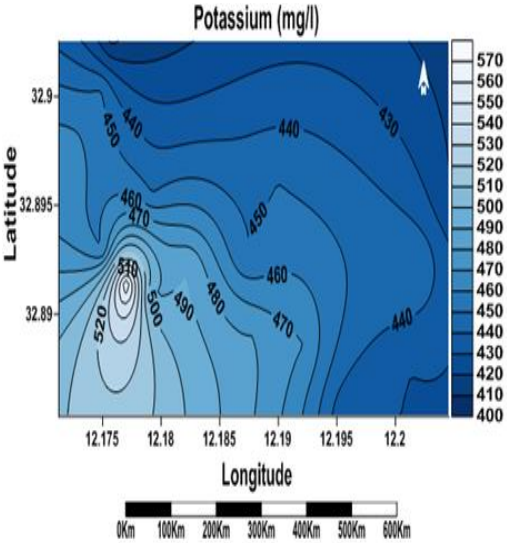


Figure 5. 20: Mg^{+2} (mgl^{-1}) at ZWDP **Figure 5. 21: $SO4^{-2}$ (mgl^{-1}) at ZWDP**
(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)



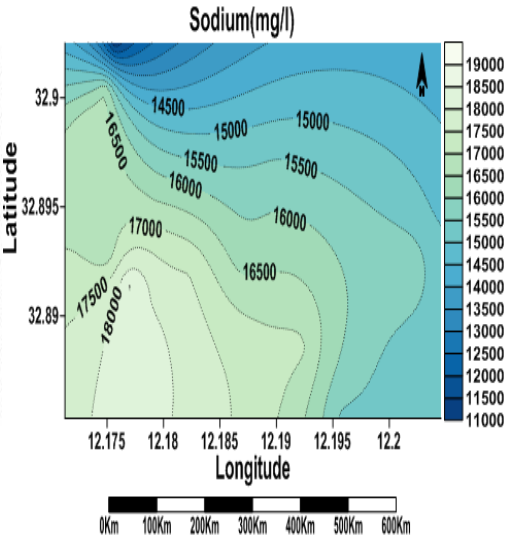
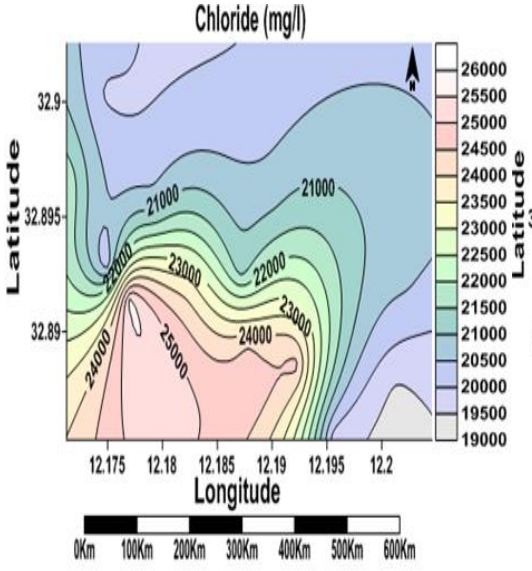


Figure 5. 22: K^{+} (mgl^{-1}) at ZWDP **Figure 5. 23: Na^{+} (mg/l^{-1}) at ZWDP**
(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

There was a wide variation in the concentration of Cl^{-}, ranging from 19,374 to 25,629 mgl^{-1}. High concentration of Cl^{-} was observed at station 50 (Cl^{-} =25,629 mgl^{-1}), while the lowest concentration was detected at station 39 and 40 (Cl^{-} =19,374 mgl^{-1}) at 8.3 m and 1.9 m depth respectively (**fig 5.24**). There was a narrow variation in the concentration of total phosphorus PO_4^{-3} (mgl^{-1}), ranging from zero to 0.177 mgl^{-1} **(fig 5.25).**



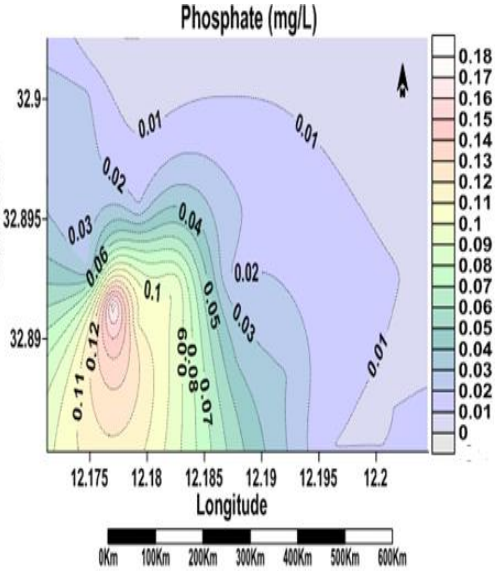
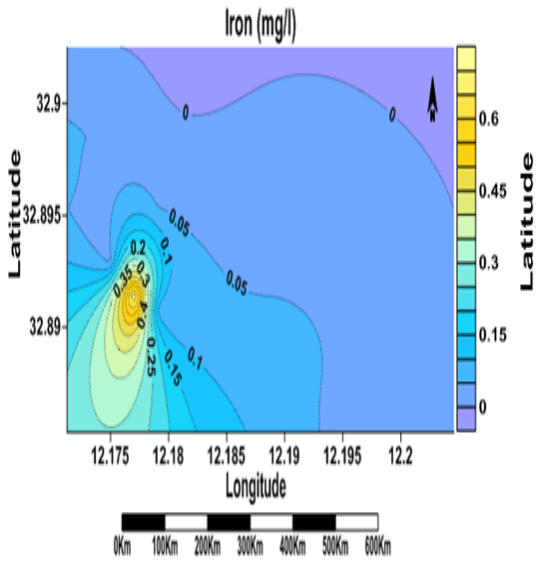


Figure 5. 24: Cl^- (mgl^{-1}) at ZWDP **Figure 5. 25: $PO4^{-3}$ (mgl^{-1}) at ZWDP**
(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

All the stations at the site revealed a narrow variation in the concentration of iron ions. Fe, ranging from zero at station 38 and station 44, with 8.4 m and 2.5 m depth respectively to 0.7 mgl^{-1} at station 50 at 0.4 m depth (**fig 5.26**). The concentration of nitrate NO_3^- showed narrow variation, ranging from zero at station 38, 42 and 44 as minimum concentration at 8.4, 4.8 and 2.5 m depth respectively to 1.15 mgl^{-1} at station 50 at 0.4 cm (**fig 5.27**).



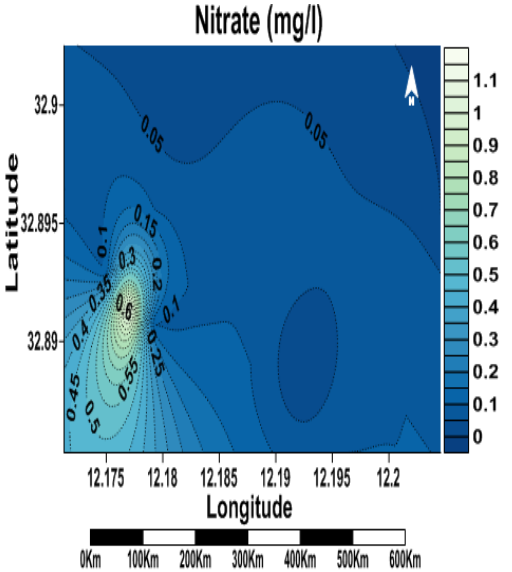


Figure 5. 26: Fe (mgl^{-1}) at ZWDP **Figure 5. 27: NO3 - (mgl^{-1}) at ZWDP**
(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

The highest temperature occurred at the surface layer, where it ranged from 25 to 37 °C at stations 38 and 50 at depth 8.4 and 0.4 m respectively, while the lowest one recorded at the seabed ranged from 23 to 35.5 °C at stations 49 and 50 at depth 0.4 m respectively **(fig 5.28 and 5. 29**).

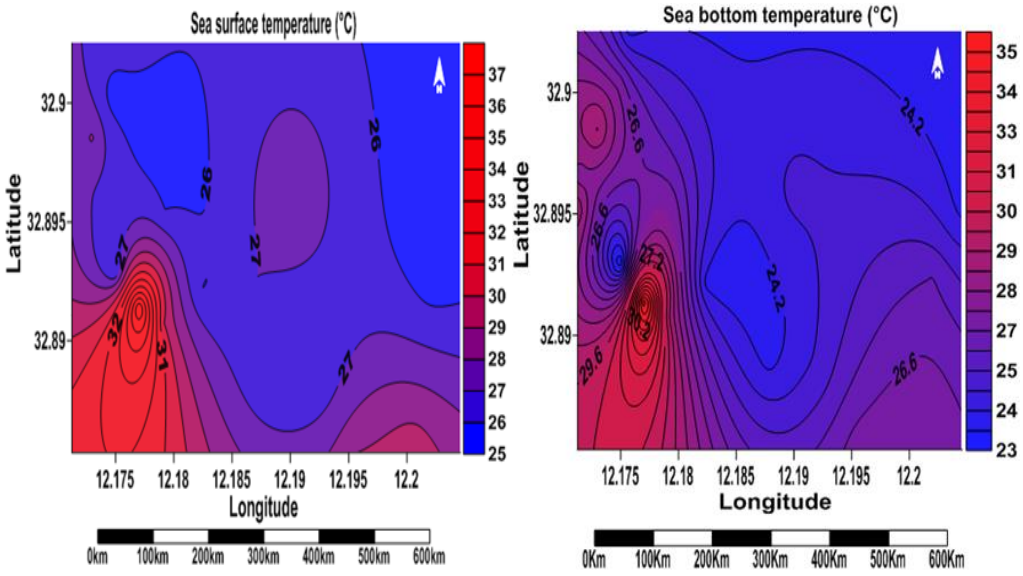


Figure 5. 28: Surface temperature (^{0}C) at ZWDP **Figure 5. 29: Bottom temperature (^{0}C) at ZWDP**
(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

The hydrogen ion concentration (pH) values revealed wide variations ranging from 7.76 to 8.46 during the study period. The minimum value was observed at station 48 with 0.6 m depth (pH=7.76) and the maximum was observed at station 41 at 2.8 m depth (pH=8.46) (**fig 5.30)**. There was a wide variation in the level of salinity ranging from 35 to 47 psu. The minimum value was observed at stations 39 and 40 at 8.3 and 1.9 m depth (Salinity=35 psu) respectively and the maximum was observed at station 50 at 0.4 cm depth (Salinity=47 psu) (**fig 5.31**).

Dissolved oxygen (DO) fluctuated between a minimum of 5.13 mgl^{-1} at station 50 at 0.4 m depth and a maximum of 8.39 mgl^{-1} at station 38 at a depth of 8.4 m (**fig 5.32**). The organic matter content level in collected sediments at ZWDP was less than 10% at each site, all the stations at these sites indicated a wide variation in the organic matter level ranging from a minimum 2.8 % at station 50 to a maximum 7.9 % at station 38 **(fig 5.33).**

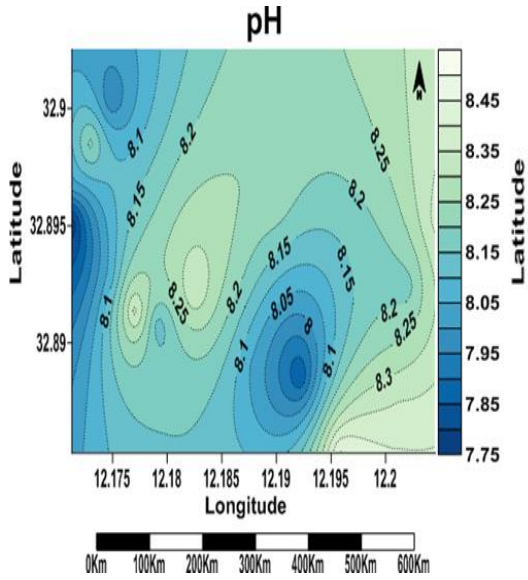


Figure 5. 30: pH at ZWDP

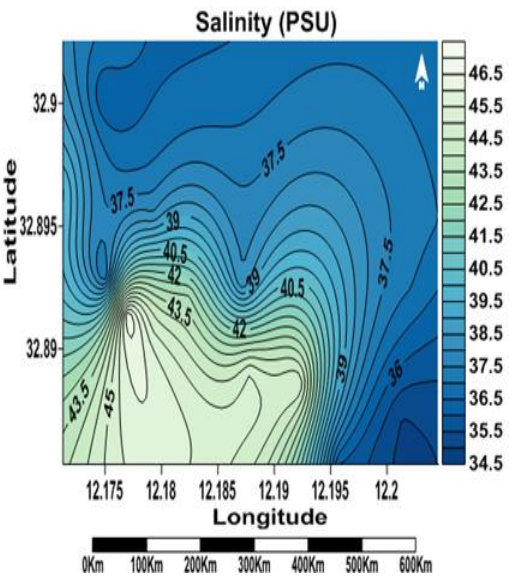


Figure 5. 31: Salinity (psu) at ZWDP

(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

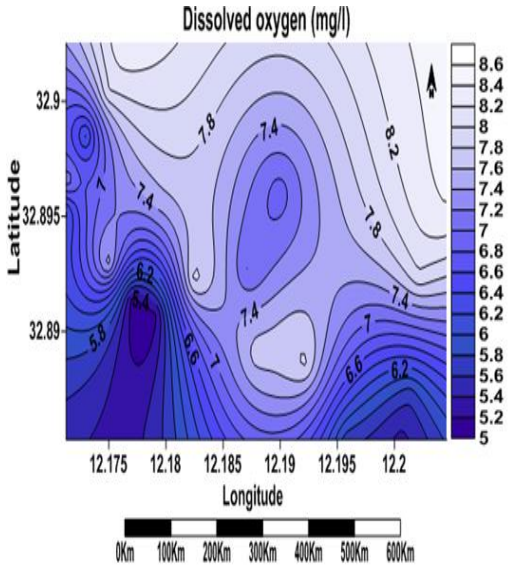


Figure 5. 32: Dissolved oxygen (DO) (mgl^{-1}) at ZWDP

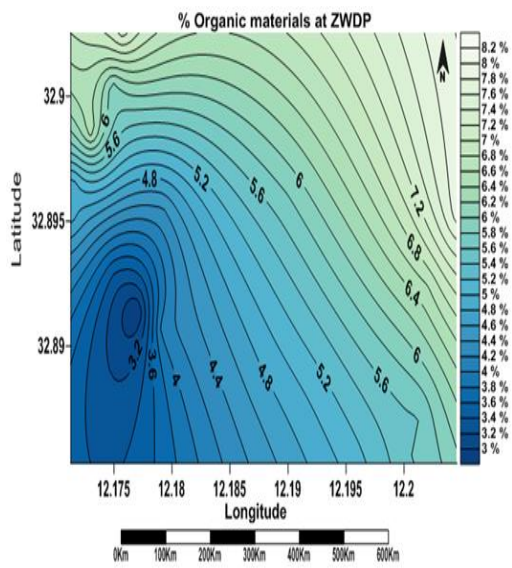


Figure 5. 33: Organic materials (%) at ZWDP

(With permission from ASCE: https://ascelibrary.org/doi/pdf/10.1061/9780784413548.224)

5.4.4. Environmental parameters at WTRIS

At WTRIS, PCA analysis was employed resulting in five components **(fig 5.34)** and the pattern is best explained in PC1 with 72.5% of the total variance, however, addition of PC2, PC3, PC4 and PC5 accounted 82.5%,89.5%,94.3% and 96.5% respectively.

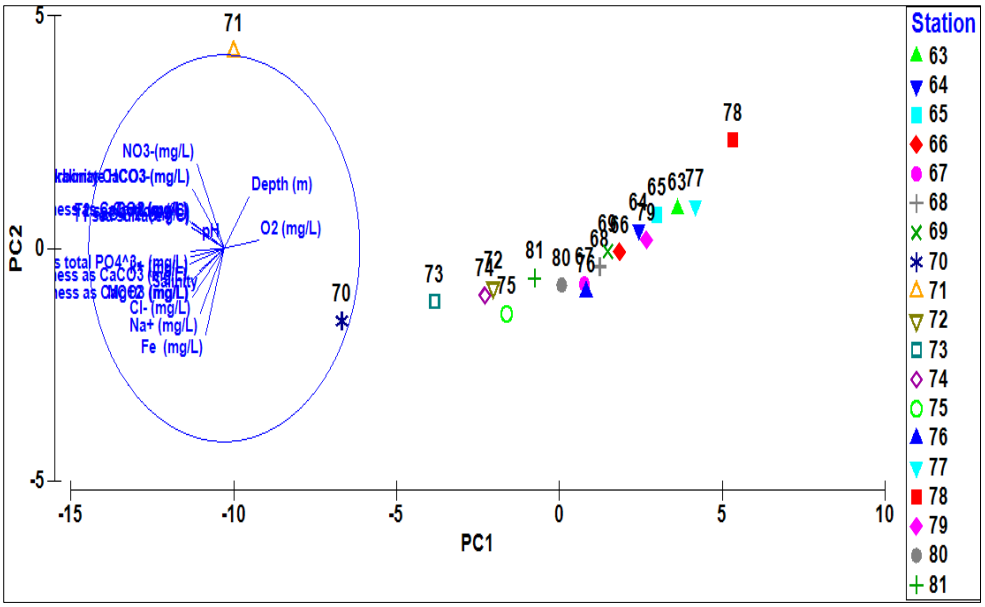


Figure 5. 34: Principal components analysis (PCA) ordination of physico-chemical parameters for WTRIS.

In PC1, the pattern between the stations is best explained with Total Hardness as CaCO3 (mg/l) (-0.3), Calcium Hardness as $CaCO_3$ (mgl^{-1}) (-0.3), Ca^{+2} (mgl^{-1}) (-0.3) and O_2 (mgl^{-1}) (0.3). In PC2 and PC3 the pattern between the stations is best explained with Depth (m)(0.3), Total alkalinity $CaCO_3$ (mgl^{-1})(0.3), Bicarbonate HCO^{3-} (mgl^{-1})(0.3), Cl^- (mgl^{-1})(-0.3), Na^+ (mg/l)(-0.3), Fe (mgl^{-1})(-0.5), pH (0.6),salinity (0.4), Na^+ (mgl^{-1})(-0.3) and Fe (mgl^{-1})(0.4). In PC4 and PC5 the pattern between the stations is best explained with depth (m) (0.3), pH (-0.7), salinity (0.4), Fe (mgl^{-1}) (-0.5), depth (m) (-0.8) and Na^+ (mgl^{-1}) (-0.3). A positive relationship between score of PC1 and seagrass percentage cover *C.nodosa* was determined using Spearman rank correlation coefficient (r_s=0.637; p=0.003) at **WTRIS**.

Seabed sediment classification of analysis of the organic content levels and the sieves for the mean grain size in (**Table 5.4 and 5.5 for WTRIS; section 5.2.3)** were categorised by the principal-component analysis (PCA) in order to determine the distribution of seabed sediment classification in area for WTRIS. At this site, PCA analysis on the Seabed sediment resulted in two components representing the mean grain size and organic material at each station (**fig 5.35**) and the pattern is best explained in PC1 with 65.4% of the total variance, however the PC2 accounted for only 34.6% of the total variance.

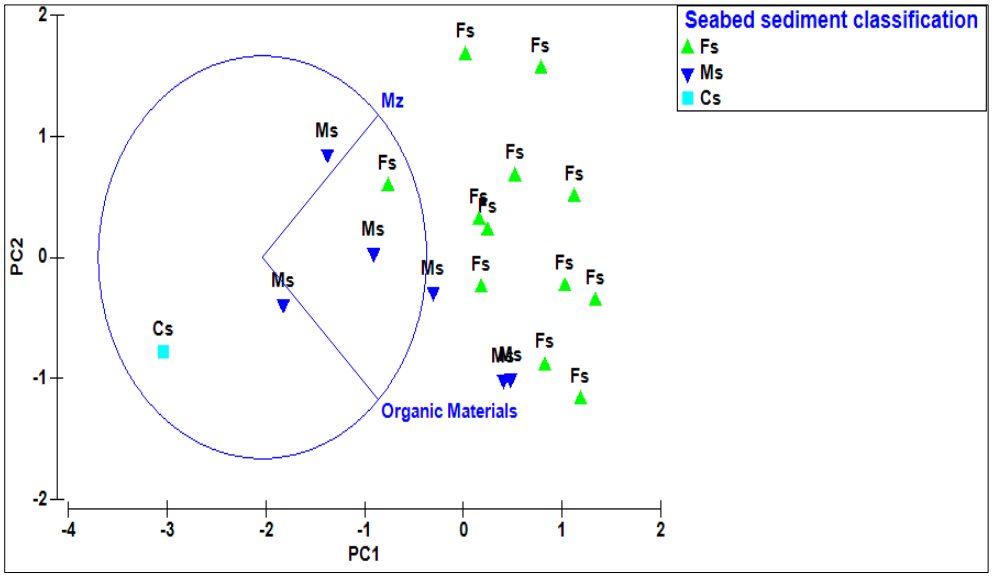


Figure 5. 35: Principal components analysis (PCA) ordination of sediment data for ZWDP: (sediment classifications: Ms= medium sand, Fs= fine sand, Cs= coarse sand).

The pattern between the stations in PC1 is best explained with organic content (g) (0.707) mean grain size (Mz) (Ø) (0.707) and in PC2 the pattern between the stations is best explained with organic content (g) (-0.707) mean grain size (Mz) (Ø) (0.707). The organic content levels which were reported in (**Table.8; section 5.2.3**) were for WTRIS (<10%) in all stations). Additionally, significant positive relationship between organic content and seagrass (*C.nodosa*) was determined using Spearman rank correlation coefficient (r_s =0.61; p=0.006), however there was non-significant a positive association between mean grain size and seagrass (*C.nodosa*) (r_s=0.405; p=0.085**)** at WTRIS.

The statistical parameters of grain size distribution have been a major factor in describing the influence of depositional processes. Generally, standard deviation and skewness are considered environmentally sensitive indicators while the mean is a reflection of competence of the transport mechanism. The results which were obtained from the sieves analysis in (**Table 5.6; section 5.2.3 for WTRIS**) shows that the mean grain size (Mz), which is reflection of the overall size of the sediment ranged from 0.70 Ø – 3 Ø (coarse - Medium - fine sand) (**fig 5.36**), while the Graphic Kurtosis (KG) was between 0.89 Ø – 2.73 Ø (platykurtic- mesokurtic-leptokurtic-very leptokurtic). Skewness (SKI) values ranged from -0.04 Ø to 0.48 Ø (strongly positive - positive -symmetrical - negative - strongly negative skewed)

while the Inclusive Graphic Standard Deviation (δI) which is a measure of sorting varied from 0.29 Ø – 1Ø (very well-well-moderately well-moderately sorted). The classification of the sediments at WTRIS show that at medium, fine and very fine sand percentage cover were higher than coarse sand.

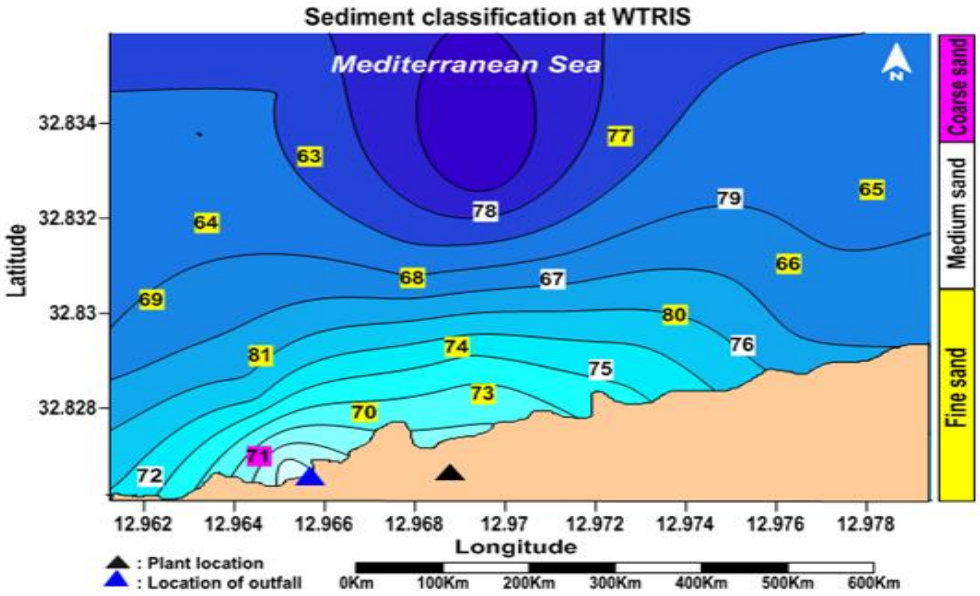


Figure 5. 36: The classification of the sediments at WTRIS

Difference in physico-chemical parameters in the seawater samples near to the outfall of WTRIS revealed that all the stations at this site have a wide variation in the level of total Hardness as $CaCO_3$ mgl^{-1}, ranging from 5,000 to 11,200 mgl^{-1}. The minimum concentration of total hardness as CaCO3 mgl^{-1} was observed at station 78 at a depth of 12 m (hardness as $CaCO_3$=5,000 mgl^{-1}) and the maximum was observed at station 71 at a depth of 0.5 m (hardness as $CaCO_3$=11,200 mgl^{-1}) **(fig 5.37).**The Ca^{+2} hardness as $CaCO_3$ mgl^{-1} in seawater at WTRIS fluctuated between a minimum of 200 mgl^{-1} at station 63, 77 and 78 at 22 m, 18 m and 12 m depth, while a maximum of 1,361 mgl^{-1} was recorded at station 71 at 0.5 m depth (**fig 5.38**). All the stations at this site showed a wide variation in the concentration of calcium Ca^{+2} ions (**fig 5.39**). The highest concentration of Ca^{+2} was observed at station 71 (Ca^{+2}=810 mgl^{-1}) at 0.5 m depth, while the lowest concentration of Ca^{+2} ions was observed at station 63,77 and 78 at the same level (Ca^{+2}=80 mgl^{-1}) at 22, 18 and 12 m depth respectively. Dissolved oxygen in seawater at WTRIS fluctuated between a minimum of 6.17 mgl^{-1} at station 71 with 0.5 m depth and a maximum of 8.96 mgl^{-1} at station 78 at a depth of 12 m (**fig 5.40**).

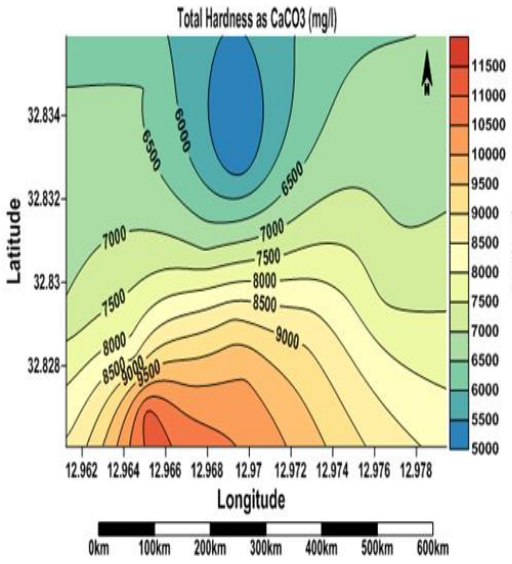


Figure 5. 37: Total Hardness (mgl^{-1}) at WTRIS

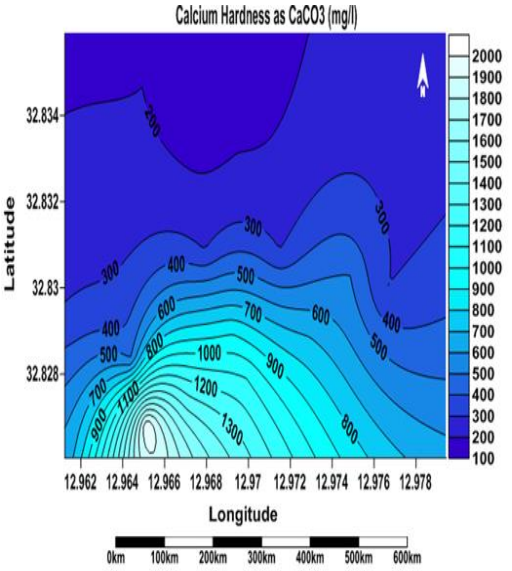


Figure 5. 38: Ca^{+2} Hardness (mgl^{-1}) at WTRIS

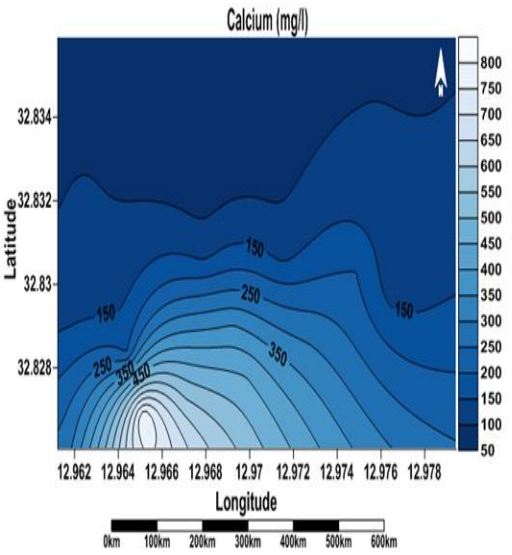


Figure 5. 39: Ca $^{+2}$ (mgl^{-1}) at WTRIS

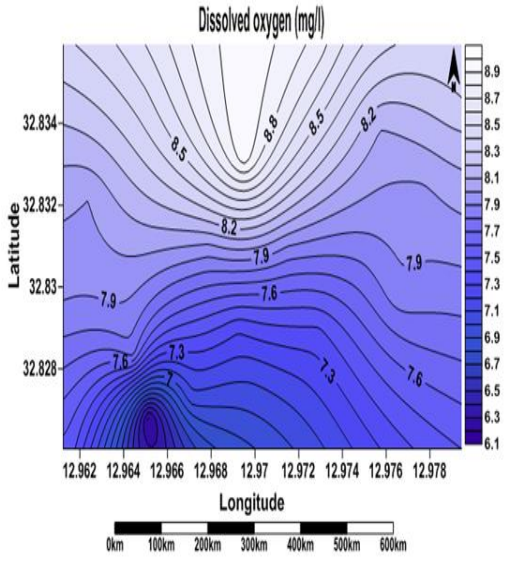
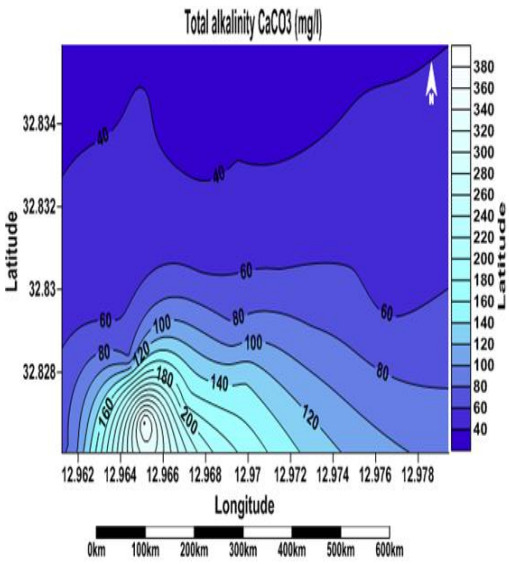


Figure 5. 40: Dissolved oxygen (DO) (mgl^{-1}) at WTRIS

The total alkalinity $CaCO_3$ (mgl^{-1}) and Bicarbonate HCO^{-3} (mgl^{-1}) value revealed wide variations, varying from 30 to 368 mgl^{-1}. The minimum value was observed at station 77 at a depth of 18 m (concentrations of total alkalinity $CaCO_3$ and Bicarbonate HCO^{-3} =30 mgl^{-1}) and the maximum was observed at station 71 at 0.5 cm depth (concentrations of total alkalinity $CaCO_3$ (mgl^{-1}) and Bicarbonate HCO^{-3} (mgl^{-1}) = 368 mgl^{-1}) (**fig 5.41**).Chloride in seawater for WTRIS is given in (**fig 5.42)**.



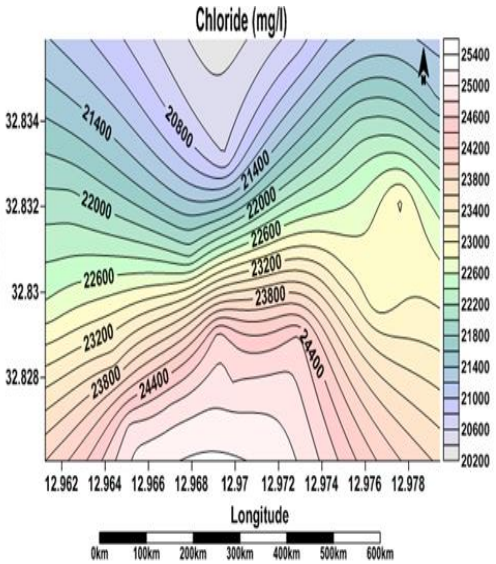


Figure 5. 41: CaCO3 and HCO-3 (mgl^{-1}) at WTRIS **Figure 5. 42: Cl- (mgl^{-1}) at WTRIS**

The present data showed that all the stations revealed a wide variation in the concentration of Cl^- , ranging from 20,617 to 24,868 mgl^{-1}. High concentration of Cl^- was observed at station 71 (Cl^- =24,868 mgl^{-1}) at 0.5 m depth, while the lowest concentration of Cl^- was detected at station 78 (Cl^-= 20,617 mgl^{-1}) at 12 m depth and 1.9 m. The concentration of sodium ions (Na^+) at WTRIS is given in (**fig 5.43**). All the stations at this site revealed a wide variation in the concentration of sodium ions. The lowest concentration of Na^+ was observed at station 78 at 12 m (Na^+ =11,680 mgl^{-1}), while the highest concentration was detected at station 71 (Na^+ =17,020 mgl^{-1}) at a depth of 0.5 m. The concentration of Fe ions in seawater at WTRIS is given in (**fig 5.44)**. All the stations at this site revealed a minor variation in the concentration of Fe, ranging from zero at station 71 and station 78 at depths of 0.5 and 12 m respectively to 0.13 mgl^{-1} at station 70 at 0.5 m depth. The vertical distribution of hydrogen ion concentration (pH) at different stations of the study area is shown in (**fig 5.45)**. The pH values revealed wide variations, ranging from 7.9 to 8.5 during the period of study. The minimum value was observed at station 67, 74 and 79 at 4.5, 2.2 and 8.5 m depth respectively (pH=7.9) and the maximum was observed at station 78 at 12 m depth (pH=8.5). The salinity data showed that all the stations revealed a wide variation in the level of the salinity content, ranging from 35 to 55 psu (**fig 5.46**). The minimum value was observed at station 66 at a depth of 10 m (Salinity=35psu) and the maximum was observed at station 70 at a depth of 0.5 m (Salinity=55 psu).

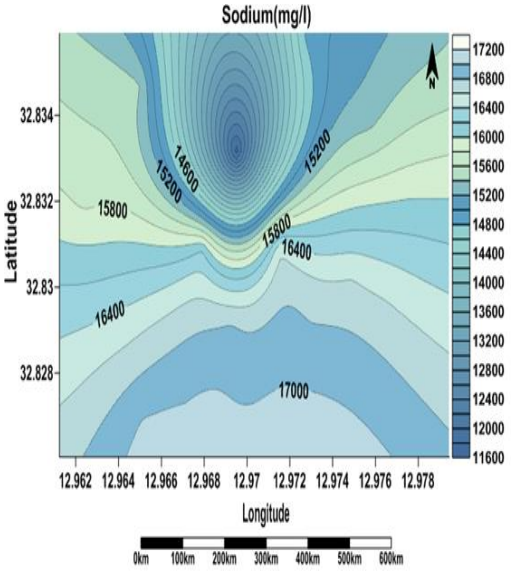


Figure 5. 43: Na^{+} (mgl^{-1}) at WTRIS

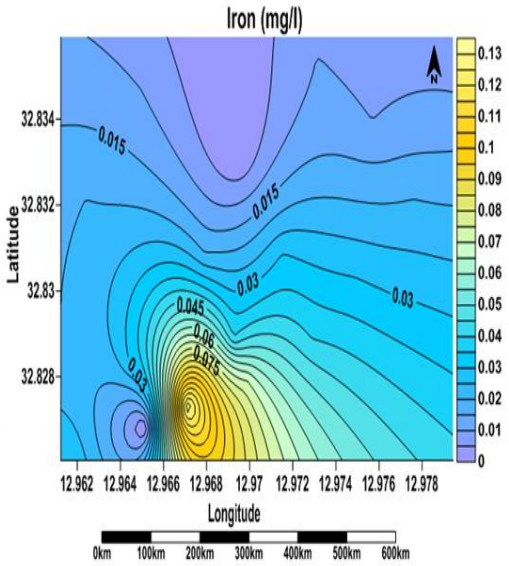


Figure 5. 44: Fe (mgl^{-1}) at WTRIS

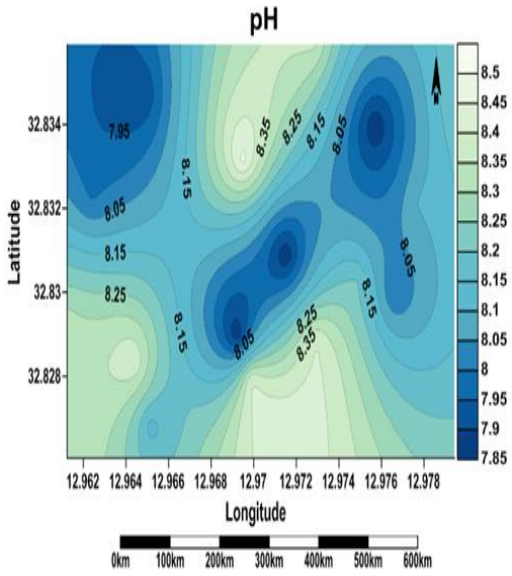


Figure 5. 45: pH at WTRIS

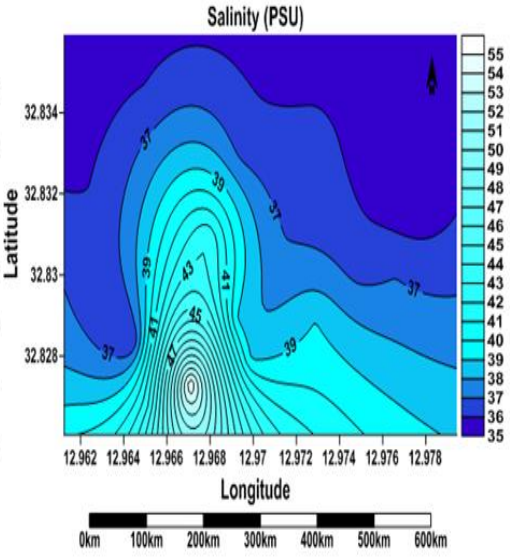


Figure 5. 46: Salinity (psu) at WTRIS

The organic matter content level in collected sediment at WTRIS was less than 10% at each site, all the stations at these sites indicated that a wide variation in the organic matter level varied from a minimum 1.04% at station 71 to a maximum 9.7% at station 77 **(fig 5.47).** Furthermore, at the two selected sites (ZWDP & WTRIS) and from the field work, it has been seen that, unhealthy seagrass was found next to the inlet pipes of ZWDP (**fig 5.48**).

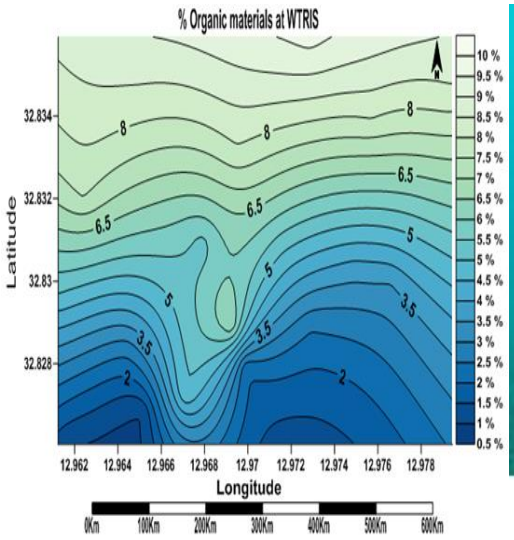


Figure 5. 47: Organic materials (%) at WTRIS **Figure 5. 48: Unhealthy seagrass next to inlet pipes at ZWDP**

Additionally polluted filamentous algae at the outfall of WTRIS were found at the end of the intertidal zone (**fig 5.49**). In addition to this, the diver who took the underwater pictures at the two sites commented that there was an effect on the leaves of the seagrass as a result of the changes in the physico-chemical constitution of the ambient seawater in the station near to the outfall (**fig 5.50; A, B and C**) compared to the seagrass found in the station further away from the outfall at both plants (**fig 5.50; D, F and G**).

Figure 5. 49: Polluted Filamentous Algae at the Outfall of WTRIS

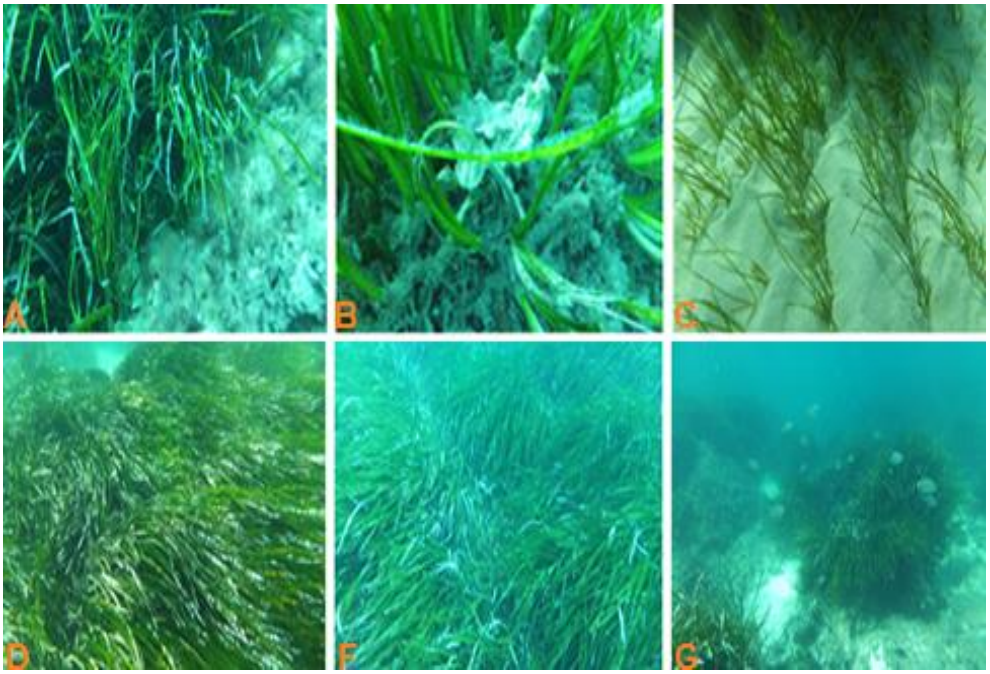


Figure 5. 50: Seagrass near and further away from the outfalls for ZWDP and WTRIS

Additionally, the emission of greenhouse gases and air pollutants, due to the energy that the desalination process required, shows clear signs of elevated levels of air pollution as a result of the use of light and heavy fuel in both plants (**fig 5.51**).

Figure 5. 51: Air pollution at ZWDP and WTRIS

5.5. Discussion

The aim of this work was to determine the physico-chemical effects of brine influx from thermal desalination plants on the marine environment. At ZWDP, eight different species were found which represented the community composition at this site (**fig 5.3; section: 5.4.1**) and included, *Posidonia oceanica*, *Cymodocea nodosa*, unknown sea algae, the brown alga *Taonia atomaria*, the red alga *Laurencia pinnatifida*, the brown alga *Padina pavonica*, the brown alga *Sargassum vulgare* and fish *Spicara flexuosa*. The community composition at stations 38, 39, 40, 42, 44, 45, 52, 53, 54 and 55 was different from stations 37, 41, 43, 46, 47, 48, 49, 50, and 51. This is due to species such as *Posidonia oceanica, Cymodocea nodosa*, unknown sea algae, the brown alga *Padina pavonica, Sargassum vulgare* and the red alga *Laurencia pinnatifida* being more abundant at station 38, 39, 40, 42, 44, 45, 52, 53, 54 and 55. The percentage cover of the brown alga *Taonia atomaria* was lower at those stations than at stations 37, 41, 43, 46, 47, 48, 49, 50, and 51. However, the community composition of those stations is represented in a high percentage cover of non-living things such as sand and sea rocks only. Additionally, the percentage cover of fish such as *Spicara flexuosa*, *Diplodus annularis* and *Diplodus vulgaris* at this site was very low and was identified only at station 45 for ZWDP. Whereas, at WTRIS only four species representing the community composition were found at this location (**fig 5.11; section 5.4.2**) and included, *Posidonia oceanica, Cymodocea nodosa,* fish *Xyrichtys novacula* and *Diplodus annularis* addition to Sea Anemone species *Anemonia sulcate*. The community composition at stations 63, 69, 77, 79 and 81 was different from stations 64, 65, 66, 67, 68, 70, 71, 72, 73, 74, 75, 76, 78 and 80. This is due to an abundance of *Cymodocea nodosa* at stations 63, 69, 77, 79 and 81. Additionally, the percentage cover of the non-living things such as sand at these stations was very low compared with stations 64, 65, 66, 67, 68, 70, 71, 72, 73, 74, 75, 76, 78 and 80 where the percentage of the sand cover at these stations was 100%. Furthermore, the percentage cover of fish such as *Xyrichtys novacula* and *Diplodus annularis* at this site was very low and was evident only at station 77 for WTRIS.

At ZWDP, the most important physico-chemical parameters that were considered include, total hardness as $CaCO_3$ (mgl^{-1}), calcium hardness as $CaCO_3$ (mgl^{-1}) and

magnesium hardness as $CaCO_3$ (mgl^{-1}), ions of calcium Ca^{+2} (mgl^{-1}), magnesium Mg^{+2} (mgl^{-1}), sulphate SO_4^{-2} (mgl^{-1}), phosphate PO_4^{-3} (mgl^{-1}), potassium k^+ (mgl^{-1}), sodium Na^+ (mgl^{-1}), chloride Cl^- (mgl^{-1}), nitrate NO^{-3} (mgl^{-1}) and iron Fe^+(mgl^{-1}) as well as sea surface and sea bed temperature , pH, dissolved oxygen DO (mgl^{-1}) , salinity (psu) and depth (m). However, at WTRIS, important parameters taken into account were, total Hardness as $CaCO_3$ (mgl^{-1}), Calcium Hardness as $CaCO_3$ (mgl^{-1}), Ca^{+2} (mgl^{-1}), total alkalinity $CaCO_3$ (mgl^{-1}) bicarbonate HCO_3^- (mgl^{-1}), chloride Cl^- (mgl^{-1}), sodium Na^+ (mgl^{-1}), iron Fe^+(mgl^{-1}), pH, dissolved oxygen DO (mgl^{-1}), salinity (psu) and depth (m).

Seawater normally has a total hardness of about 6,500 mgl^{-1} as $CaCO_3$, with a calcium hardness of about 1000 mgl^{-1} as $CaCO_3$ and a magnesium hardness of about 500 mgl^{-1} as $CaCO_3$ (Boyed and Tucker, 1998). However, at ZWDP a very significant difference of (- 500 to + 9,071 mgl^{-1}), (- 800 to + 361 mgl^{-1}) and (+ 5,300 to + 1,370 mgl^{-1}) respectively has been recorded. The ion concentration of calcium Ca^{+2} (mgl^{-1}), magnesium Mg^{+2} (mgl^{-1}), sulphate SO_4^{-2} (mgl^{-1}) , potassium k^+ (mgl^{-1}), sodium Na^+ (mgl^{-1}) and chloride Cl^- (mgl^{-1}) in Mediterranean seawater typically ranges from (440 to 670 mgl^{-1}), (1,371 to 1,550 mgl^{-1}), (2,400 to 2,965 mgl^{-1}), (410 to 620 mgl^{-1}), (10,105 to12, 000 mgl^{-1}) and (21,000 to 23,000 mgl^{-1}) (Ladewig and Asquith, 2011) respectively. However, in ambient seawater at ZWDP, a very significant difference in the ion concentration of calcium Ca^{+2} (mgl^{-1}), Mg^{+2} (mgl^{-1}), sulphate SO_4^{-2} (mgl^{-1}) , potassium k^+ (mgl^{-1}), sodium Na^+ (mgl^{-1}) and chloride Cl^- (mgl^{-1}) has been recorded as follows; (- 306 to - 216 mgl^{-1}) (+ 37 to + 1,900 mgl^{-1}), (- 1,400 to + 1,183 mgl^{-1}), (- 408 to - 570 mgl^{-1}), (+ 945 to + 6,550 mgl^{-1}) and (- 1,626 to + 2,625 mgl^{-1}) respectively. While, at WTRIS, a very significant different in a total hardness as $CaCO_3$ (mgl^{-1}), a calcium hardness as $CaCO_3$ (mgl^{-1}) , a calcium Ca^{+2} (mgl^{-1}) , sodium Na^+ (mgl^{-1}) ions and chloride Cl^- (mgl^{-1}) has been recorded as follows; (- 1,500 to + 4,700 mgl^{-1}), (- 800 to + 1,000 mgl^{-1}), (-360 to + 131 mgl^{-1}), (+ 1,575 to + 5,080 mgl^{-1}) and (+ 35 to + 1,868 mgl^{-1}) respectively.

Water hardness $CaCO_3$ is essentially a measure of the amount of dissolved calcium and magnesium in the water body and animals and plants need these minerals to live. Calcium is a vital component in the cell walls, shells and bones of many

aquatic organisms and magnesium is similarly essential in chlorophyll, used by green plants to photosynthesize. Hardness mitigates the toxicity of metals and calcium and magnesium ions help prevent fish absorbing metals such as lead, arsenic and cadmium, through their gills. The greater the hardness, the more difficult it is for toxins to be absorbed. When hardness equals alkalinity, the only cations present in significant concentrations in water are calcium and magnesium (Murphy, 2014). Low calcium levels, coupled with other environmental factors that affect osmoregulation, can cause problems for marine organisms, for example, when the pH and salinity is low or high (Boyed and Tucker, 1998).

Stanley (2006) also reported that the growth rates of aragonitic codiacean algae *Penicillus and Halimeda* reduced when Mg^{2+}/Ca^{2+} ratio reduced. Hence, increases in the level of total hardness ($CaCO_3$) close to the desalination plants (ZWDP and WRTIS) may be due to dosing levels of anti-scale agents and utilization of sponge-ball cleaning used for controlling acidification of seawater (Soror, 2009). The solubility of inorganic salts that form scale ($CaCO_3$, $CaSO_4$, $Mg(OH)_2$) decreases with increasing temperature. The scale formed on the surfaces reduces the overall heat transfer coefficient, thus decreasing the efficiency in the production of stations (Wildebranda et al., 2007). Addition of anti-scalants caused more CaCO3 to be discharged with the brine and may have an adverse effect on the marine species

Further to this, it was found that the sulphate ions concentration in the marine environment were higher at ZWDP. This may be due to sodium sulphite being injected into the feed water line for the boiler, which is necessary in thermal desalination plants to remove the dissolved oxygen from the steam boiler (Oil and Water Supplies Limited, 2006).When the sulphite oxidises into forms of sulphide, this could be harmful because the high concentration of sulphide in the sea sediment can harm seagrasses, since sulphide is a plant toxin inhibiting respiration (Borum et al., 2004), which may drive ecosystem level alterations in animal and plant distribution. Howarth and Teal (1979) reported that due to huge amounts of sulphates in seawater, breakdown of organic matter often is consumed by sulphate reducing bacteria that release free sulphide ions into the sediments. This release may also intoxicate marine plants and organisms. Short-term increase in sediment sulphide levels can affect the balance between seagrass photosynthesis and

respiration while long-term increase may reduce the rate of photosynthesis of sea grass leading to other effects and plant death (Gwada, 2004).

Moreover, the results show that the concentration levels of sodium and chloride ions were higher at the two plants which are possibly due to the addition of sodium hypochlorite. This is because in most distillation plants, the intake seawater is chlorinated continuously by dosing with a sodium hypochlorite solution for the disinfection process at a certain dosing rate (Verdier, 2011). This means more chemical-additives and more chemicals are discharged into the sea. Chlorine is hazardous to the marine environment and marine resources (Hashim and Hajjaj, 2005).

Seagrasses are salt tolerant even when it exceeds the concentration in the seawater. Specifically, seagrasses accumulate sodium (Na^+), chloride (Cl^-) and Potassium (K^+) but balance Na^+ and Cl^- fluxes to maintain osmotic equilibrium and prevent its accumulation within the cytoplasm (Morenoa et al., 2014; Exadactylos, 2015). A study by Khalafallah et al., 2013 shows that accumulation of Na^+ under brine stress was accompanied by a reduction in seagrass health, leading to high mortality rates. High apoplastic levels of Na^+ and $C1^-$ alter aqueous and ionic thermodynamic equilibrium, resulting in hyperosmotic stress, ionic imbalance, and toxicity. Thus, it is vital for the plant to re-establish cellular ion homeostasis for metabolic functioning and growth (Niu et al., 1995). Na^+ may have adverse effects on plant catabolism and metabolism, whereas K^+ is essential for maintaining osmotic balance and acts as co-enzyme in biological reactions. Hence, uptake of K^+ is vital for the general health and growth of plants (Touchette, 2007). However, Na^+ has been reported to compete with K^+ for intracellular influx. As a result, many K^+ transport systems tend to have high affinity for Na^+ allowing them to function as Na^+/K^+ transporters (Khalafallah et al., 2013). In essence, Na^+ levels may therefore inhibit the efficiency of K^+ in marine plants (Mottaleb, 2013). This study also showed a significant positive correlation between the level of N^+ and Cl^- at the two selected sites and also major positive correlation between the levels K^+ and Na^+ at ZWDP.

Similarly, phosphate, iron and nitrate ions concentrations in seawater typically range from 0.088 mgl^{-1}, 0.0034 mgl^{-1} and < 0.1 mgl^{-1} (Anthoni, 2006) respectively.

However, a difference of (+ 0.068 to + 0.1 mgl^{-1}), (0 to + 0.6966 mgl^{-1}) and (0 to + 0.15 mgl^{-1}) respectively has been recorded in ambient seawater at ZWDP. Whereas, at WTRIS, a very significant difference of (0 to + 0.1266 mgl^{-1}) in iron ions has been recorded.

Phosphates are required in pre-treatment processes as chemical additives, such as Tri-sodium phosphate, which is used to control pH and conductivity for the boilers in thermal desalination plants (Les, 2015). Increased levels of phosphate and nitrate ions may cause the eutrophication of the receiving seawater. It also leads to algal growth **(fig 5.49),** which, depending on the degree of eutrophication, can develop severe environmental effects on the marine environment (Davis, 2015). In addition to this, it was found that the iron ions concentration in the marine environment at WTRIS is slightly higher. This may be due to backwash processes which result in the phenomena of reddish brine at the discharge point further to the corrosion phenomena in thermal desalination plants which depends on the alloys present in the process line (Lozides, 2015). Further to its co-location with West Tripoli Power Plant established in 1976 (Ahwide and Aldali,2013), all the brine disposed from power boilers is mixed with WTRS (desalination plant), so the reddish brine near to the outlets of desalination plants will lead to increased turbidity of the seawater thereby affecting marine species**.**

Seawater normally has a total alkalinity $CaCO_3$ ranging from 100 to 500 mgl^{-1} (Student Watershed Research Project, 2014), however at WTRIS a very significant difference of (- 70 to - 130 mgl^{-1}) respectively has been recorded near to the outlet of the plant. Similarly, bicarbonate HCO_3^- (mgl^{-1}) ions concentration in Mediterranean seawater typically ranges from 120 to 161 (mgl^{-1}) (Ladewig and Asquith, 2012), while in ambient seawater at WTRIS, a very significant difference of (- 90 to + 207 mgl^{-1}) has been recorded.

In thermal desalination plants, fouling is carried out by scaling with calcium carbonate or carbonate, calcium sulphate and magnesium hydroxide (Elsaid et al., 2012). The variation in the ions released by fouling in thermal desalination plants is due to the evaporation process inside heat exchanger units. MED or MED-TVC plants usually operate at temperatures between 63 -75 °C known as top brine temperature (TBT) and due to solubility problems, thermal desalination plants

operation is generally limited to TBT. The formation of the alkaline scaling ($CaCO_3$ and Mg $(OH)_2$) has been found to depend on temperature, pH, concentrations of HCO_3^-, CO_3^{-2}, Ca^{+2}, Mg^{+2} ions as well as the rate at which CO_2 is released (Marie, 2010; Anezi and Hilal, 2007). Most of these substances are discharged with the brine into the marine environment, while CO_2 is released into the air impairing air quality due to the vacuum process in the evaporator's cell, thus CO_2 lowers the pH when dissolved in seawater making the ocean more acidic. Coral reefs, calcareous plankton and other organisms whose skeletons or shells contain calcium carbonate may be particularly affected as a result of decreases in carbonate ions (Caldira and Wickett, 2003). Not only that, acidification of the oceans may also threaten oceanic food chains (Dean, 2009) affecting marine ecosystems in general. Further increases in the level of CO_2 emissions may result from the use of heavy fuel in thermal desalination plants at both sites, which have been indicated at both sites (**fig 5.51)**.

Seawater temperature profiles were studied on the Libyan coastline by the Marine Biology Research Centre in 2006. The sea bed and the sea surface varied from 13.6°C to 28°C (Bonanno et al., 2006). However, at ZWDP results showing differences as +15.4°C to +3°C respectively above ambient seawater temperature near to the outlet were recorded. However, the results show that at WTRIS there is no significant difference in seawater temperature in the period of study. Connor et al., (2007) reported that seawater temperature can influence the population, community and species level of marine organisms due to fluctuations in seawater temperature around both sites.

Normally, seawater pH is slightly alkaline and it ranges from 7.9 to 8.4. This range is created through a balance between biological activity and seawater (Owens, 2009). However, this study results show differences as - 0.14 to + 0.06 near to the outlet of ZWDP, while, at WTRIS, the results show that, the pH value was at the same value ranging from 7.9 to 8.4, which has been recorded in ambient seawater. The changes in the pH value may be due to the salts which are discarded with the brine into the marine environment, because in most thermal desalination plants, alkaline scales from heat exchanger surfaces are typically removed by washing with warm acidic seawater. Furthermore, the use of chemical inhibitors such as benzotriazole derivatives (Abuzinada et al., 2008), being added to protect the plants

from corrosion may also be hazardous to aquatic life. A wide cross-section of aquatic animals thrives in an environment of pH level ranging between 6.5 and 8.00. Outside this range, the diversity may be reduced because it damages the physiological system of most organisms and can reduce reproduction. Low levels of pH can also allow toxic elements to become more available for uptake by aquatic plants and animals. This can produce conditions that are toxic to aquatic life (Faragallah et al., 2009) and the constant of pH value at the same level at WTRIS may be due to the strong wave current of seawater at the period of study. The results also indicates that the presence of marine species was found to be at a low density in both sites near to the outfall of the desalination plans. This decrease could be attributed to a reduction of pH levels which affected their diversity and forced the marine species to migrate to other zones (Mabrook, 1994) which were more conducive to their healthy existence.

Dissolved oxygen levels in seawater in the eastern coast of Libya have been studied by Jack *et al*., (2009) and found to be between 9.8- 10.5 mgl^{-1}. However, the results at ZWDP show a very significant difference of - 4.67 to - 2.1 mgl^{-1}. In contrast, at WTRIS, the results show a difference of - 3.65 to -1.54 mgl^{-1} near the outlet. This is possibly due to increases in brine temperature inside the cells/ stages of the units as thermal desalination plants produce potable or industrial water when it reaches top brine temperature (TBT) (World Health Organization, 2005). In order to reduce the temperature, the brine is blended with cool water of the sea, but as the amount of salts and thermal energy increases, the amount of dissolved oxygen decreases which will have an impact on the physico-chemical state of the receiving seawater. Also, de-aeration and the use of sodium sulphate as an oxygen scavenger in the brine recycle line is used to control corrosion inside the units which could limit the amount of dissolved oxygen. (Abuzinada et al., 2008; Environmental International Consultants 2009). The recommended minimum concentration of DO in marine water is 8.0 mgl^{-1} and any reduction beyond this level may have lethal and sub-lethal effects in a variety of organisms particularly in fish (Canadian Council of Ministers of the Environment, 1999).

The seawater salinity of the Libyan coast is ≤ 37.8 psu (Placenti et al., 2013) and the difference of (- 2 to + 9.2 psu) and (- 2 to + 6 psu) in the ambient seawater

salinity near the outfall of ZWDP and WTRIS respectively was recorded. Marine organisms commonly are only able to cope with a narrow variation in salinity in their habitat (North et al., 1995). Salinity thresholds and variations also affect the composition of the marine ecosystem in a mixohaline environment by constraining colonisation, germination and species richness (Joyce et al., 2005). Increasing salinity around the ZWDP and WTRIS outlets is attributed to high temperature, which is due to cooling water and consequent evaporation and the high concentration of salts associated with the discharged water. Furthermore, during the study period, the depth was obvious as an indicator to the marine biodiversity at both sites, the lower depth stations near to the outlets of the plants were poor in the biodiversity level compared to the stations located forward of the discharge points from the plants.

The sediment data analysis which is shown in the physical analysis of the two sites (**fig.5.15 and fig. 5.36; section 5.4.3 and 5.4.4)** indicate that, at both sites medium, fine and very fine sand percentage cover was higher than coarse sand, therefore this study suggests that the sediment along the coastal water has been transported by strong sea currents suggesting that fine sand is initially shifted, followed by medium sand and ultimately the heavier coarse sand. In addition to the results which are displayed (**Table.5.4; section 5.2.3)** for the organic matter levels at both sites reveal that the organic matter content level in the sediments was < 10%. The organic matter levels can affect the aquatic ecosystem by interacting with inorganic matter to form complex compounds, which include in its structure several elements. Organic matter is initially produced by the fixation of inorganic carbon dioxide by marine phytoplankton in the euphotic zone, and released into the water column by decomposition of dead cells. The high abundance of organic content level in the selected area compared to other locations is probably due to the chemical additives used in desalination processes such as anti-scale, that are commonly added into the feed water (seawater) and the main components of antiscalants are organic (Lattemann,2005; Abdelwahab and Hamoda,2012). Sediment quality can also affect the growth and distribution of seagrasses (Morrision and Greening, 2015), and the seagrass photosynthesis can also affect sediment metabolism through the release of organic substrates by seagrass roots (Calleja et al., 2006).

The presence of seagrass beds plays a prominent ecological role and supports the productivity on which many communities of marine animals feed and reproduce further to enhance stabilization of the sediment such as *P. oceanica* and *C.nodosa*, which have been used as bio-indicators in the Mediterranean Sea and in Libya, as they are considered one of the most suitable biological indicators for water quality in order to assess the status of Mediterranean waters. Thus, the importance of taking these species as indicators of quality of the marine environment seems paramount (Benkhayal, et al., 2013).

P. oceanica and *C.nodosa* were included in the red list of threatened marine species of the Mediterranean Sea (Montefalocne et al., 2005) as a result of increasing the amount of industrial pollutants into the marine environment. Thermal desalination stations directly impact the marine environment by returning the relatively high temperature concentrated brine to the sea. Although data that documents the effects of the brine disposal from desalination plants is very scarce, it is now clearly documented that, especially in the Mediterranean region, seagrass such as the *P. oceanic*, an endemic plant in the Mediterranean Sea is very sensitive to high salinity derived from hyper-saline desalination effluent (Laspidou et al.,2010). Additionally, this increases seawater salinity, water currents, turbidity and temperature. These in turn deteriorate the marine environment and cause fish to migrate (Al Mutaz, 2013). Further to this, study in Egypt by Mabrook, 1994 shows that, most of the coral reefs, planktonic organisms and fish species have declined and even disappeared as a result of changes in the physico-chemical parameters in ambient seawater near to outlets of desalination plants as a result of brine discharge.

Therefore, the outcome of this study suggests that at both sites that were chosen as selected areas of study, a significant positive correlation was observed at ZWDP and WTRIS between the biological data and physico-chemical parameters which demonstrates the impact of brine disposal from ZWDP and WTRIS on the marine environment. Additionally, a significant positive correlation between the organic content levels in the sediments and seagrass was also detected at ZWDP and WTRIS and non-significant positive correlation coefficient between mean grain size and sea grass at both sites. The significant positive correlation indicates that a positive linear association and increased physico-chemical parameters of brine has

caused profound changes in the physico-chemical parameters of seawater and an effect on abundance and composition of the marine organisms. Hence, these results are consistent with previous studies, which found similar responses in the marine species exposed to the brine disposed from distillation plants.

5.6. Summary

To sum up, it can be said that chapter five provides the results methodology regarding the brine influx from thermal desalination plants into the Libyan marine environment, with particular references to ZWDP and WTRIS on the Libyan coastline. The brine influx from both distillation plants into the marine ecosystem releases chemical residues and thermal energy which negatively affect the marine ecosystem. An increase in concentration of a number of ions and compounds from discharged brine indicates an alteration in the physico-chemical properties of the seawater. Moreover, as most of the Libyan thermal desalination plants are run by heavy fuel, there is an indication that it is likely to cause future ocean acidity, as a result of CO_2 emissions. Also, the brine has low pH and a high alkalinity which may lead to an increase in ocean acidification which is supported by the high amounts of hardness in terms of calcium and magnesium ions and other compounds. In addition, the high salinity and temperature of brine may have a negative effect on the marine organisms as the cell osmolarity (salinity) and enzyme functioning (temperature) may be compromised. Lastly, as the Libyan government plan to increase the production capacity of their desalination plants, this means more brine disposal into the sea which has the potential to degrade the physico-chemical characteristics of the marine ecosystem. There are a number of proposals for solutions to the problems caused by the discharged brine, which have led to extending the scope of this chapter, allowing us to respond quickly to minimize any possible negative effects by using the solutions which are presented into the next chapters.

Chapter Six: On-site sodium hypochlorite generation from brine disposal of distillation plant

6.1. Introduction

Seawater provides the optimum source for desalination technology as an inexhaustible source with high motility, making it the best medium for industrial use. However, its composition includes dense components, such as algae, slime and bacteria, which can cause biological fouling and blockage of the inlet structure of desalination plants and other related equipment. This is further exacerbated by a warm climate where microbial activity thrives in warm humid regions (Saleem, 2011). Furthermore, operational problems are affected by biofouling of heat exchanger surfaces, particularly in desalination and power stations, resulting in compromised heat transfer efficiency, additional operating and maintenance expenditure and increased fluid frictional resistance in the piping system (Murthy et al., 2005).

The majority of desalination plants, e.g. thermal distillation or reverse osmosis, have been designed with a hypochlorination unit to inject sodium hypochlorite at the seawater intake to inhibit further biological growth of potential contaminants such as algae, within the connecting pipeline to onshore facilities (Roux et al., 2015; Voutchkov, 2013). It is well documented that chlorine, which is normally electrochemically generated on site, is a very effective chemical widely used for a range of coastal applications. Once seawater is electrolysed to generate sodium hypochlorite, it results in a safer, more robust and cost effective option than the use of purchased chlorine gas, which tends to disintegrate into oxygen and chlorates which can form trihalomethanes (Saleem, 2011; Abdul and Weshahi, 2009; Choi, 2013).

Along with UV sterilisization, ozone or biocide, chlorine is a valuable disinfectant. However, it can be volatile in liquid or gas form when in transit, or during a period of storage, hence the need for it to be generated on site (Saleem, 2011; Xu et al, 2010). It is expedient to electrochemically generate oxidation agents used for water treatment on, or as near as possible to, their application location and it needs to be carefully monitored because chlorine-containing oxidisers have high oxidation

activity and are considered to be one of the most powerful disinfecting agents (Bashtan, 1999).

As the scarcity of global water increases, particularly in warmer climes, the development of desalination technology can overcome this serious issue. Although the production of brine expelled from desalination plants can pose a threat to the marine environment (Al-Barwani and Purnama, 2007), it has now been disclosed that this could be a valuable by-product for on-site generation of hypochlorite. (Abdul and Weshahi, 2009)

Taking these considerations into account with the results obtained in chapter five, focussing on the Libyan coastline distillation plants in the Southern Mediterranean Sea, an integrated production scheme is needed to safeguard this technology in order to create a synergy between the process and further use in commercial and industrial sectors, while protecting the marine environment and outlying areas. Ultimately, this chapter aims to investigate the production of sodium hypochlorite (NaOCl) from an electrochemical cell fed by brine in a controlled environment on site. The study will also discuss the effects of various critical operating parameters on this process, including, electrode materials, production of sodium hypochlorite (NaOCl), inter-electrode spacing, applied current density, energy and power consumption further to determine the price of utilizing the brine by using the electrochemical method.

6.2. Sodium Hypochlorite Production Techniques

6.2.1. Chemical Method

Chloride is made to react with a solution of sodium hydroxide resulting in the production of sodium hypochlorite, sodium chloride and water, as illustrated in following equation:

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

This method produces highly concentrated solutions, but their properties are contra-indicative for alternative uses (Ronco and Mishkin, 2007).

6.2.2. Electrochemical Method: On-site generation of NaOCl

Sodium hypochlorite is formed by electrolysis of sodium chloride found in seawater or brine solutions in a controlled environment. Exothermic chemical reaction is caused by an electrical Dc current applied to the seawater that flows through an electrolyser, fitted with customised electrodes resulting in conversion to sodium hypochlorite solution (NaOCl). Sodium chloride NaCl is broken down into sodium ion Na^+ and Chloride ion Cl^- as a result of Dc electrolysis of an aqueous solution of sodium chloride, as illustrated in following equation:

- At the anode, free chlorine is generated

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

- At the Cathode, hydrogen evolves with corresponding formation of hydroxide ions (OH^-)

$$2H_2O + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

OH^-ions, migrate from the cathode area and react with sodium (Na^+) and chloride (Cl_2) near the anode, thus producing sodium hypochlorite (NaOCl) and the overall reaction can be written as following:

$$2NaOH + Cl_2 \rightarrow 2NaOCl + H_2$$

The composition of seawater presents a high percentage of hardness ions resulting in the presence of certain substances such as calcium, magnesium and other metals from hydroxide and carbonates. These solidify and are removed from the electrolyser by seawater stream. Meanwhile, certain cathodic deposits that remain on the surface need to be chemically cleaned periodically (Thangappan and Sampathkumaran, 2008).

6.3. Study site

This study was conducted in September 2015 on the Libyan coastline around the brine disposed from Zwuarah distillation plant (ZWDP) as presented in chapter five (**fig 5.1**).

6.3.1. Experimental procedure

A small square basin measuring 25 cm in length, width of 20 cm and depth 15 was fabricated at the workshop of ZWDP to assess the sodium hypochlorite production capability of the prototype cell from brine disposed. The basin is made from glass with a thickness of 4 mm. The glass plates were pasted together by using silicon, then five electrode materials (Graphite, Copper, Aluminium, Titanium, Zirconium) were chosen for this experiment with a dimension of 10 cm long, 5 cm width and 5mm thickness, and then weighed prior to the experiment, using sensitive electronic scales.

The electrodes were immersed in the brine and connected to adjustable variable DC power supply 0-30V and 0-10A (Mastech). For each experiment applied, 0.0021 m^3 of brine was utilised for at least 100 min in the cell for each electrode material. The USB camera (HUE HD) was connected to a Toshiba laptop by USB cable and focussed on the electrochemical cell in order to monitor the reaction **(fig 6.1).** For each type of electrode material, the inter electrode spacing was altered from 2 cm, 4 cm and 6 cm respectively in order to evaluate the efficiency production of NaOCl cell. The chemical characteristics of the brine used in this experiment have been presented in **table 5.3 in chapter 5**.

Figure 6. 1: Electrochemical cell for brine utilizing

6.3.2. Sampling and data collection

Brine samples were collected from the electrochemical cell every 20 minutes in order to measure the free chlorine, which presented NaOCl concentration using Hach method 8021 (**see appendix 6)**. Additionally, a 1 µl in each batch was examined by using DPD Free Chlorine Reagent Powder Pillow according to Hach method for water, wastewater and seawater.

Cost analysis of utilizing the brine converted to NaOCl is one of the most salient factors that influences the application of an electrochemical process. Additionally, the cost of electrode and other accessories of the cell needs to be considered. The major operation cost is the current density, energy and power consumption during operation in the electrochemical process. The current density was calculated by dividing the electric current by the effective surface area of the electrode (**Eq. 6.1**), energy and power consumption were evaluated by (**Eqs. 6.2 and 6.3)**. The electrodes (anode and cathode) were weighed by using sensitive electronic balance in order to evaluate the deposits on each electrode after each experiment has run.

- $J = I/A$…… (**6.1**)
- $E = \left[\frac{I*U*T}{V}\right] \div 1000$…… (**6.2**)
- $P = E/T$…….....(**6.3**)

Where, E is Energy consumption needed to reuse the brine into the form of NaOCl (kW.h/m^3), I is the total electric current (Ampere), U is the total electric voltage (V), T is the time in hours, V: is the volumetric of brine need to be treated into NaOCl (m^3), J: Current density (A/cm^2), P is Power consumption (kW) and T is the time in hours (Hsu et al., 2015; Cyprtaa et al., 2013; Joseph and Sharma, 2012).

Results revealed insignificant production of NaOCl when using copper, aluminum, titanium and zirconium electrodes. Therefore, only graphite electrodes have been discussed and all the outcomes from this study are presented in (**Table 6.1** and **6.2**)

Table 6. 1: Results of Using Graphite Electrodes from Electro Chemical Cell

Inter-Electrode Spacing	Time (Min)	Cl^- (ppm)	V (v)	U consumption (V)	I (A)	I consumption (A)	J (mA/cm^2)	Time (hours)	E= (I×U×T)/V (W.h/m^3)	E= (I×U×T)/V(Kwh/m^3)	P=(E/T) (kw/ m^3)
	20	573	8.00	22.0	7.00	3.00	0.060	0.33	10,476	10	31
	40	617	8.10	21.9	7.10	2.90	0.058	0.67	20,162	20	30
2 cm	60	630	8.30	21.7	7.30	2.70	0.054	1.00	27,900	28	28
	80	1860	8.40	21.6	7.50	2.50	0.050	1.33	34,286	34	26
	100	2140	8.50	21.5	7.60	2.40	0.048	1.67	40,952	41	25
	20	572	8.40	21.60	7.20	2.80	0.056	0.33	9,600	10	29
	40	676	8.49	21.51	7.40	2.60	0.052	0.67	17,754	18	27
4 cm	60	850	8.78	21.22	7.47	2.53	0.051	1.00	25.565	26	26
	80	2311	8.80	21.20	7.50	2.50	0.050	1.33	33,651	34	25
	100	2600	9.00	21.00	7.60	2.40	0.048	1.67	40,000	40	24
	20	350	9.00	21.00	8.30	1.70	0.034	0.33	5,667	6	17
	40	450	9.20	20.80	8.38	1.62	0.032	0.67	10,697	11	16
6 cm	60	532	9.30	20.70	8.50	1.50	0.030	1.00	14,786	15	15
	80	1490	9.40	20.60	8.60	1.40	0.028	1.33	18,311	18	14
	100	1790	9.50	20.50	8.70	1.30	0.026	1.67	21,151	21	13

Table 6. 2: Graphite Electrode Corroded at Inter Electrode Spacing 2, 4 and 6 cm

Types of electrodes	Spacing: 2cm		Spacing: 4 cm		Spacing: 6 cm	
	Anode (+)	Cathode (-)	Anode (+)	Cathode (-)	Anode (+)	Cathode (-)
Original mass (g)	42.8982	43.0665	42.9835	42.618	43.551	43.533
Mass after test (g)	43.0507	43.3933	43.1245	42.8442	43.661	43.7233
Difference (g)	0.1525	0.3268	0.14	0.2262	0.11	0.19

6.4. Results and discussion

An electrochemical technique was applied to produce sodium hypochlorite using the brine disposal from ZWDP. While assessing the performance of graphite, copper, aluminum, titanium and zirconium electrodes, results revealed that production of NaOCl for graphite electrodes (MCCA 1.82 gr/m^3) was significant, in contrast to copper and aluminum which, despite being good conductors and commonly used in the electrolytic industry (Saleem, 2011), were insignificant.

With reference to titanium and zirconium electrodes, low process efficiency for the generation of NaOCl prove them to be unsuitable for brine utilisation. Titanium is used as a cathode material within the electrochemical industry to produce chlorates and hypochlorite from seawater (Asokan and Subramanian, 2009). According to a

study by Saleem et al., 2012 results show that a titanium electrode coated with a dimensionally stable anode (DSA) revealed excellent stability production of NaOCl from seawater. However, the titanium applied for utilizing the brine was grade one and uncoated and the fact that the salinity of the brine was higher than seawater contributed to an insignificant production of NaOCl.

Moreover, when using zirconium electrodes, the generation of NaOCl was minimal as attested by Laˇcnjevaca et al., (2013) who discovered that zirconium oxide decreases the hypochlorite reduction rate somewhat. This may be due to the high salinity of the brine produced from ZWDP. The energy consumption for the electrodes such as copper, aluminium, titanium and zirconium during the experiment run was nil, which is due to a polarization phenomenon, which counteracts and lowers the efficiency of electrochemical processes (Sivasankar, 2008).

Graphite electrodes showed excellent stability after a period of 60 min, the production of NaOCl rose concomitantly around 2,140, 2,600 and 1790 ppm at inter electrode spacing 2cm, 4cm and 6cm respectively**.** Graphite is generally used in the electrochemical industry for both cathode and anode materials in electrochemical cells for producing NaOCl (Rivera and Matousek, 2015). Additionally, inter-electrode spacing plays an important role in an electrochemical process with respect to process efficiency.

The variation in NaOCl production with reaction time at different inter-electrode spacing ranged from 2cm, 4cm and 6cm for graphite electrodes as plotted in (**fig 6.2).** Results showed that the maximum production of NaOCl was achieved at a spacing of 4 cm, while minimizing the electrode inter spacing at 2cm increases the process efficiency, compared to inter electrodes spacing at 6cm.

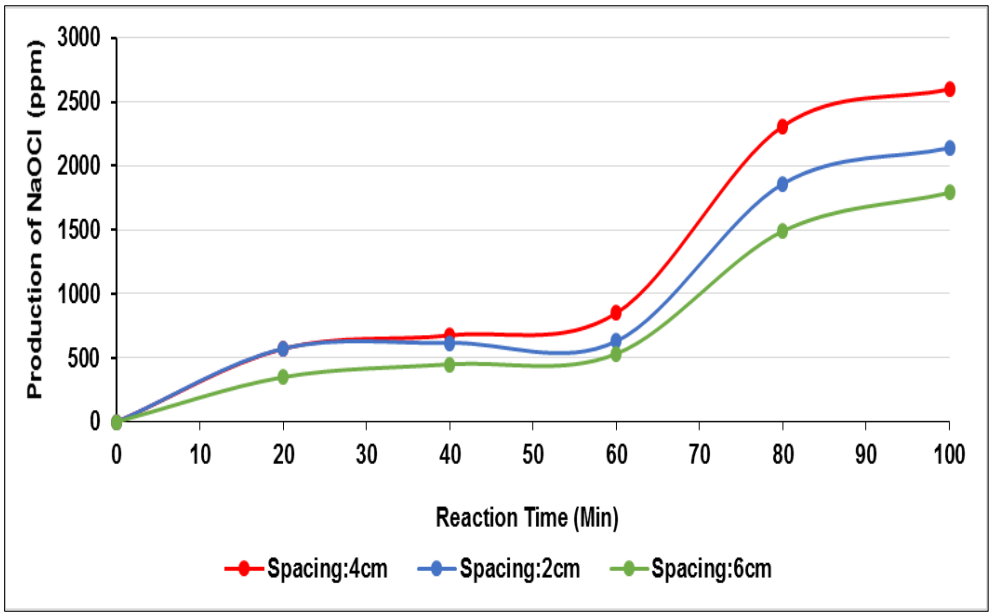


Figure 6. 2: Variation in NaOCl Production Using Graphite Electrodes

According to Faraday's initial law of electrolysis, production of sodium hypochlorite depends on the density and amount of electric current passed through a brine solution (Alagha, 2010). Therefore, the current density on the production of NaOCl using graphite electrodes was investigated by using mathematical equation (**Eq. 6.1).** The production of Sodium hypochlorite has been plotted against current density in (**fig 6.3, 6.4 and 6.5)** at different gaps between the electrodes.

Results indicated that the production of NaOCl increased gradually, whereas the current density decreased steadily in electrochemical cell with variations between (0.060-0.048 mA/cm^2), (0.056-0.048 mA/cm^2) and (0.034-0.026 mA/cm^2) at inter electrode spacing 2cm,4cm, and 6cm respectively. The reduction in the production of NaOCl and increase of the current density is likely due to an increase in temperature of the brine in the start-up of the reaction time (Alagha, 2010), however, the lower current at 100 min is maybe due to the increase in the oxygen evaluation (Nylén, 2008) as a result of a higher concentration of HOCl and OCl^- (Burney et al., 1999). According to results obtained using a current density of 0.048 mA/cm^2, at 4 cm, this was found to be most suitable for an efficient process of utilizing the brine to produce NaOCl.

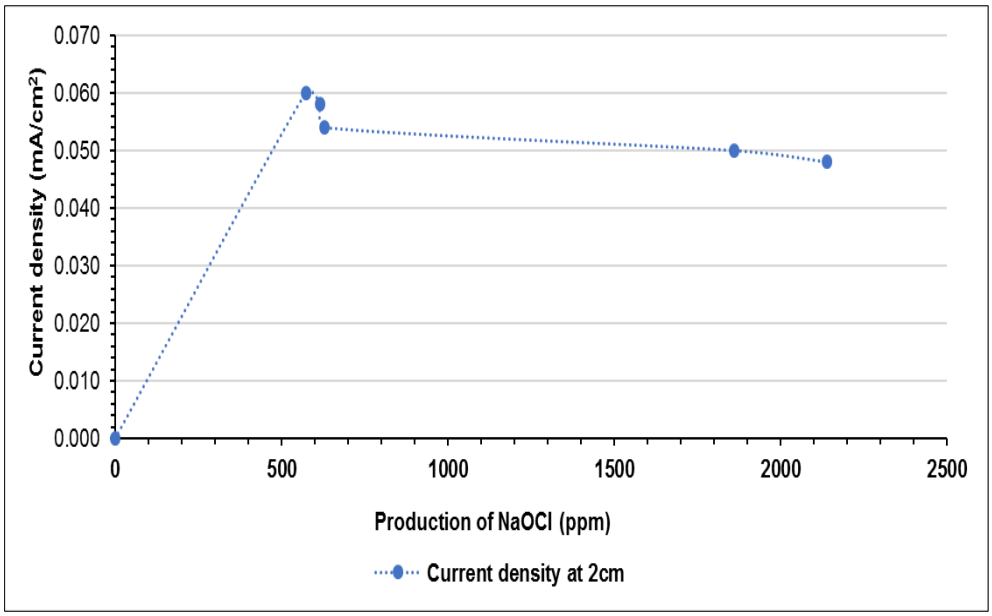


Figure 6. 3: NaOCl Production and Current Density at 2cm

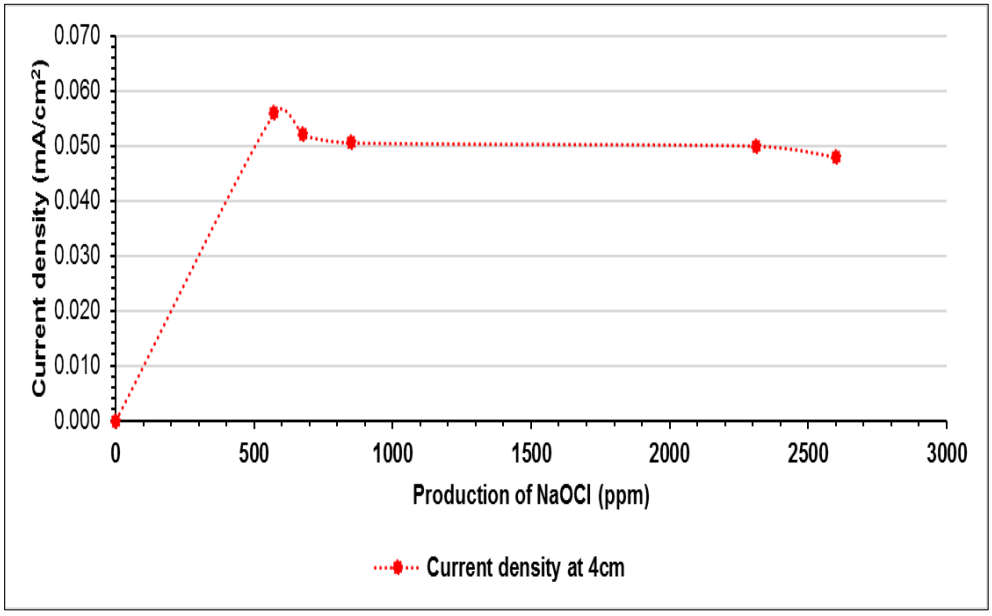


Figure 6. 4: NaOCl Production and Current Density at 4cm

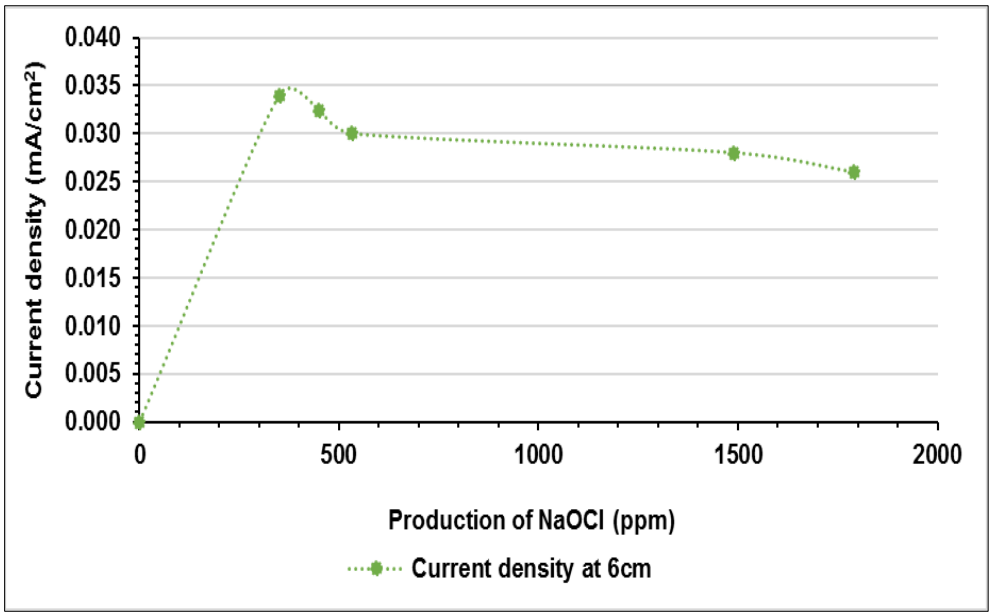


Figure 6. 5: NaOCl Production and Current Density at 6cm

The results from (**fig 6.6, 6.7 and 6.7)** also show that as the electric current passing through the cell gradually weakened, there followed an increase in energy consumption with higher NaOCl production, because more electrolytes were electrolyzed over time. This generally improves the process efficiency, as the performance of electrochemical cell process has been evaluated by using (**Eq. 6.2)**, it was observed that a decrease in inter electrodes spacing can intensify energy consumption, thereby improving the production of NaOCl which is consistent with the literature (Hsu et al., 2015).

At inter electrode spacing 2 cm and 4 cm with an electrolysis time up 100 min, the energy consumption was higher (ranging from 10 to 41 kw.h/m^3 and from 10 to 40 kw.h/m^3 respectively with higher NaOCl production (ranging from 573 to 2140ppm and 572 to 2600) respectively than at inter electrode spacing 6cm which ranged from 6-21 kw.h/m^3 with NaOCl production varying from 350 to 1790 ppm. Thus, widening the gap between electrodes reduces the capital and energy consumption cost, but may compromise the treatment efficiency for brine utilization.

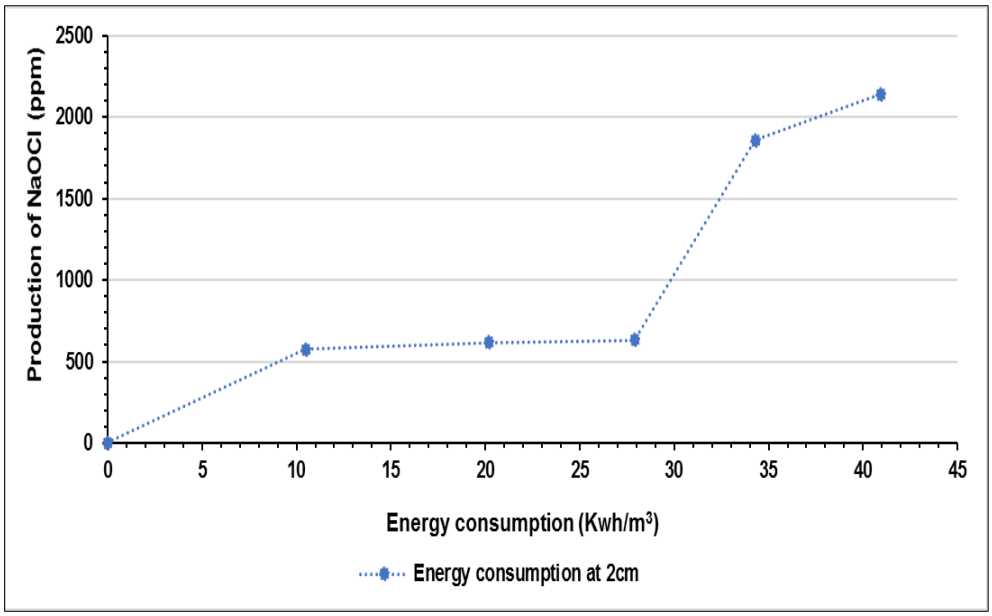


Figure 6. 6: NaOCl Production and Energy Consumption at 2cm

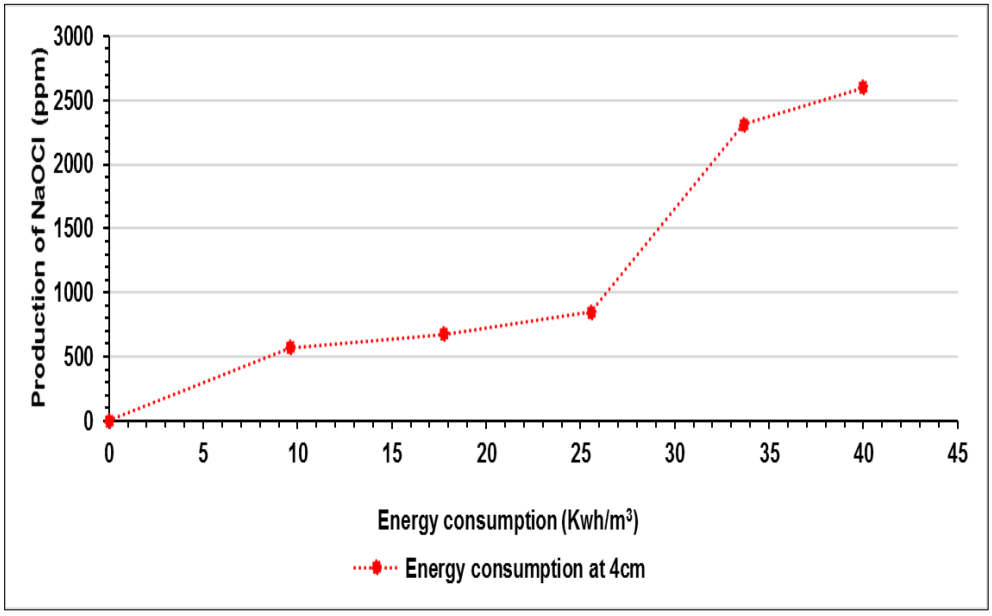


Figure 6. 7: NaOCl Production and Energy Consumption at 4cm

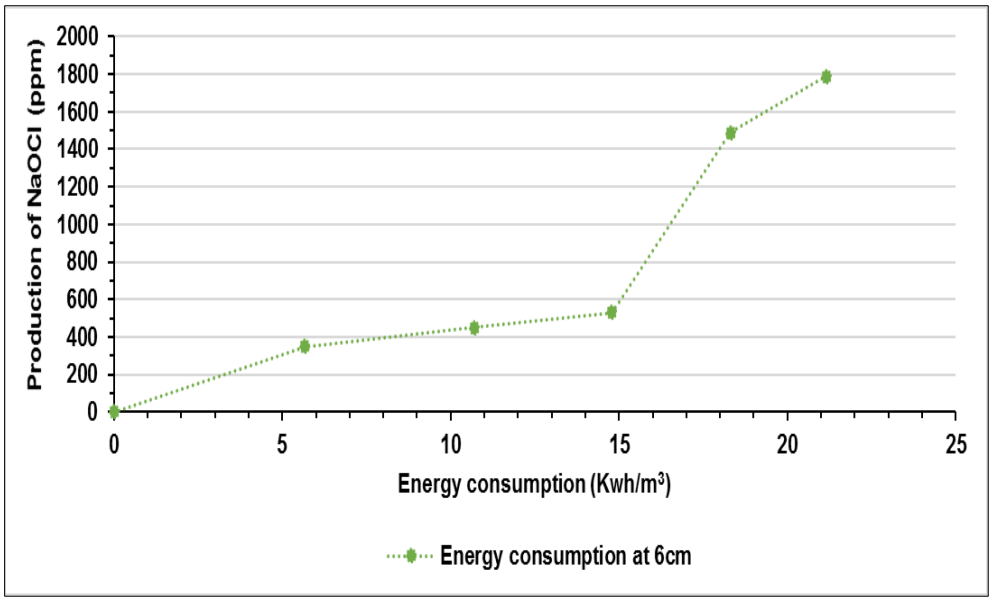


Figure 6. 8: NaOCl Production and Energy Consumption at 6cm

From (**Eq.6.3),** it was also observed that as the reaction time increases, the power consumption declines in (**fig 6.9)**, while on the other hand decreasing the cost of utilizing the brine. At inter electrode spacing 2 cm and 4 cm, the power consumption was higher, with a greater concentration of sodium hypochlorite generation varying between 10-25 kw/m³ (573-2140ppm) and 29-24 kw/m³ (572-2600ppm) than at inter electrode spacing 6cm 17-13 kw/m³ (350-1790). It is therefore important to select an optimum level of energy consumption in order to achieve an economical process for utilizing the brine.

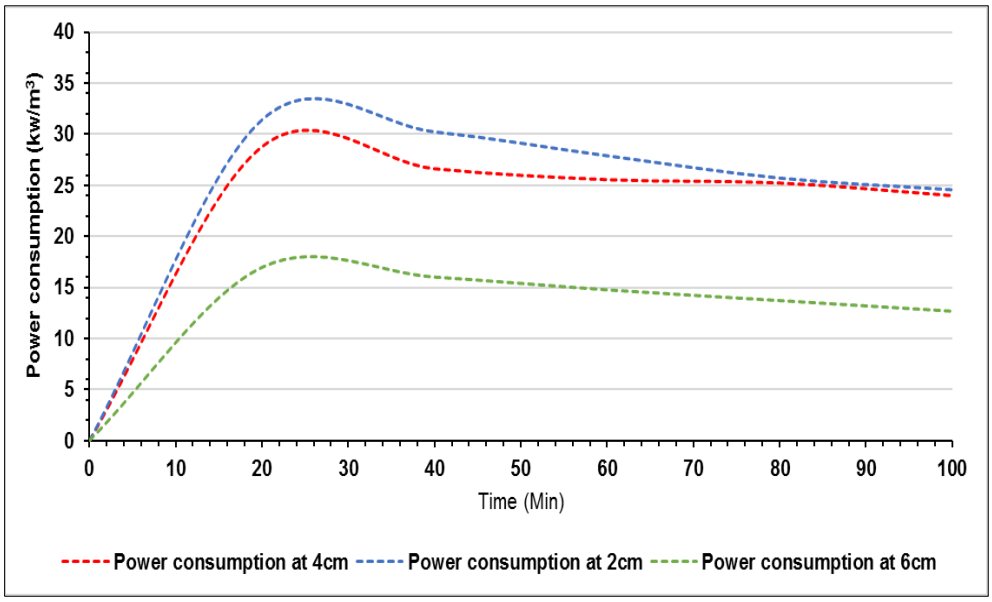


Figure 6. 9: NaOCl production and contact time at different inter electrode spacing

The consumption of the electrode material is also directly related to the economics of the electrochemical process. Consumption rates of electrode materials were measured using the difference of the weight before and after the reaction time in **(fig 6.10)**. The results reveal that the mass electrode materials accumulated during the reaction time for brine utilization was lower at anodes (0.15 gr, 0.14gr and 0.11gr) than cathodes (0.33gr, 0.23gr and 0.19gr) for graphite electrodes at inter electrodes spacing 2cm, 4cm and 6cm respectively. This may be due to alkali hydroxide, which accumulates at the cathode, in addition to the evolution of hydrogen gas occurring at the cathode, as asserted in the literature (Thangappan and Sampathkumaran, 2008; Rabah et al., 1991). Hence, the choice of electrode material for brine utilisation is a key factor in achieving optimum results in conditions of high salinity.

The cost of utilizing brine disposed from distillation plant in the form of NaOCl can be estimated from the lab scale work. As the tariff of kilowatt hour of power consumption for the heavy industrial sector in Libya is $ 0.30 (General Electricity Company of Libya, 2014), thus the cost of sodium hypochlorite yield of 2600 ppm at 24 kw/ m^3 is expected to be 7.2 $/$m^3$.

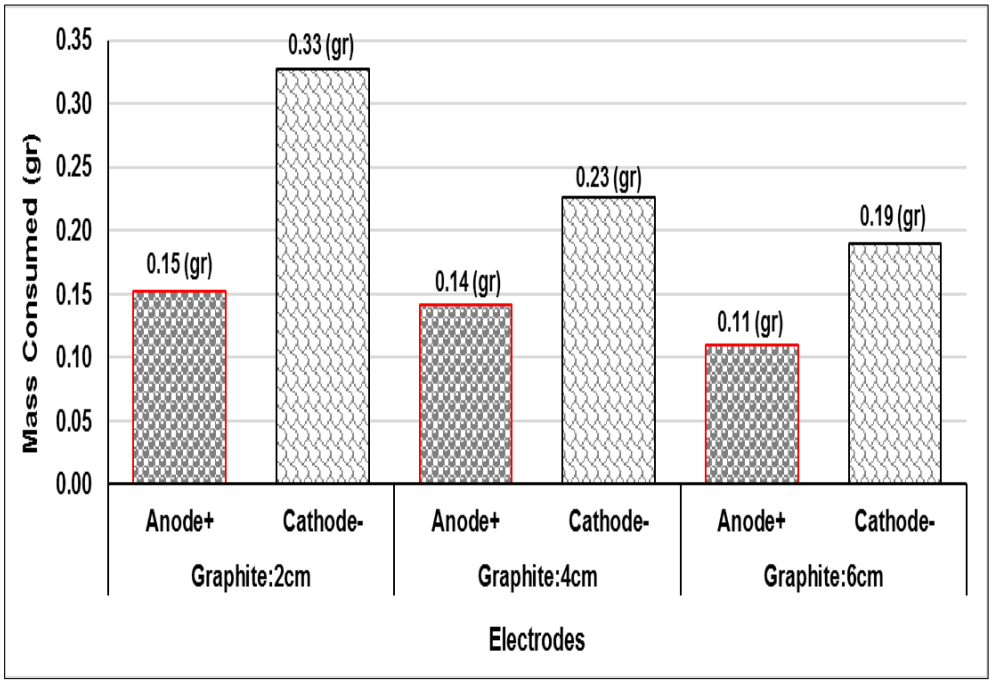


Figure 6. 10: Consumption Rate of Electrodes in the Cell for NaOCl Production

6.5. Summary

According to experimental work in this chapter, it can be concluded that brine has many favourable properties when considering the environmental and cost factors pertaining to coastal desalination plants. On-site production of sodium hypochlorite is deemed to be advantageous for further development of distillation when specialised units can be connected to brine flow.

After testing different types of electrodes, graphite showed high stability in performance, producing sodium hypochlorite to a value of approximately 2,600ppm. Furthermore, having a 4cm gap between electrodes with current density of 0.048 mA/cm was a crucial factor in terms of good process economy, in contrast to inter electrode spacing of 2cm and 6cm. Consequently, use of brine fed into the hypochlorination unit should optimise the current input, the DC voltage and appropriate reaction times in order to achieve optimum results.

Another by-product from electrochemical reaction is hydrogen which can be collected for further use, thereby reducing operating costs of hypochlorination units. In addition, the performance of the electrochemical unit can be improved by mixing brine disposal from distillation plants and using different electrode materials, such as titanium electrode coated with a dimensionally stable anode (DSA) mesh thereby optimising cost efficiency while minimizing residual deposits on the electrodes. Another option for reducing the cost of brine utilisation could be the use of alternative power supply by the hypochlorination unit such as solar energy, which is widely available in Libya. Hence, the next chapter will investigate the use of this in evaporation ponds.

Chapter Seven: Salt production by the evaporation ponds of brine disposed from distillation plant

7.1. Introduction

The production of salt has long been an established global business since the 4th century millennium in Europe (Olivier and Kovacik, 2006), the first century in China (Flad et al., 2005) and similarly in Central America (Andrews, 1983). Libya experienced the introduction of salt trading routes in the 5th century (Batterson and Boddie, 1972). Without salt, human civilisation could never have evolved, as it is integral to the development of a society. It has a huge impact on all life forms, man has used solar evaporation or saltmarshes to produce this valuable mineral since the dawn of time (Korovessis and Lekkas, 2009).

Approximately 200 million tons of sodium chloride are manufactured in solar saltworks (marais salants, salinas, saltfields, salzgärten, solnitzi) annually representing one third of the total amount internationally produced (Davis, 2000). The solar process of evaporating brine remains the main activity in coastal regions, to produce salt (Akridge, 2008). This focuses on wetland areas, particularly in salt marshes that provide optimum conditions in terms of biodiversity and eco-systems (Kavakli et al., 2006; Deegan et al., 2012), that are key to environmental factors (Dardir, 2006). A huge range of flora and fauna exist and survive in salt marshes and solar saltworks areas providing bio-diversity, while enhancing the improvement of water management and flood prevention (Moosvi, 2006). In the southern coastline of the Mediterranean Sea, especially in Libya, there are plentiful salt marshes bordered by sabkhas. A prominent sabkha, located in the western part of the country is Abu Kammash Salt Marsh, which produces 120,000 tons of sodium chloride annually from its marine salt operations (El-Magsodi and Haddoud 2010). Until now, the production of marine salt in Libya has been affected by a lack of technical expertise and equipment, combined with pressures of global competition and the need for environmental integration (Mohammed, 2003).

Evaporation ponds are constructed to separate the salt from the brine waste by a process of natural evaporation. They are predominantly used as a storage area of brine that has been rejected from desalination plants (Thomas, 2009), and offer a

viable solution for plants located inland, specifically reverse osmosis, where the costs of brine management are high (Glueckstern and Priel, 1997; Arnal et al., 2005). These plants produce much more concentrated waste brine than thermal desalination plants, which reject diluted amounts because of the ambient seawater temperature and use of cooling water that is normally mixed with brine prior to disposal (World Bank, 2012; Darwish et al., 2013).

In both scenarios (reverse osmosis and thermal desalination technologies), the water produced has a higher salinity concentration than the source water. In cases of reverse osmosis and thermal desalination, the brine discharged contains chemical residues of antiscalants, while the by-products of biocides and antifoaming agents are present in brine discharged from thermal desalination plants. A low concentration of metals results from the corrosion phenomenon at different levels in both reject streams (Lattemann and Höpner, 2008). The average dose of antifoam agent injected into the make-up seawater is 0.1mg/l (Darwish et al., 2013), while the maximum dose of antiscalants agent is 2 ppm in thermal desalination plants (Abdulgader and Mustafe, 1998). Neither of these commercial chemical additives pose any threat to the environment or food grade products (Cipollina et al., 2012). The seawater intake is also chlorinated with typical doses 0.5–2 mg/l of active Cl_2 (Darwish et al., 2013). Because of the extended process within each evaporator and a high temperature, any residual effects of the brine discharge are minimal due to high dilution following reaction within the evaporation units (Cipollina et al., 2012). However, there is an impact on sensitive ecosystems and the marine environment because of high salinity and continuous disposal (Lattemann and Höpner, 2008; Medeazza, 2005).

During the desalination process, there are various concentrations of salts and minerals found in brine including SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, K^+, Fe^{2-} and Cu^{2+} (Abdulsalam et al., 2016). The exploitation of these salts and minerals has sparked interest among scientific communities. Recent literature has revealed that the use of standard methodologies for exploiting sodium chloride NaCl (halite) can be used alongside brine recovery processes in thermal desalination plants, reaping considerable benefits (Ravizky and Nadav, 2007; Hajbi et al., 2010).

Evaporation ponds provide the optimum solution for dealing with reduction of potable water costs by minimising brine volumes and reducing the environmental impact of the desalination process (Cipollina et al., 2012; Rodríguez et al., 2012) due to benefits gained from processing solid waste that produces a decontaminated liquid flow which is easier to use than original waste (González et al., 2012). The construction of ponds is not labour intensive, or costly in terms of maintenance and operation and does not require specialist equipment, thus being the best option, given the location properties of high aridity, high evaporation rates, low rainfall and land costs (Ahmed et al., 2000). Furthermore, they offer benefits of providing areas for aquaculture practices, e.g. fish breeding *Artemia salina or algae cultivation of Dunaliella salina for the production of β-carotene*) as well as recovery of poor quality waters while producing energy through solar ponds (Delanuez et al., 2012; Rodríguez et al., 2012). One of the key issues regarding the use of evaporation ponds for brine disposal is potential seepage of brine through the soil, which can cause contamination while raising salinity levels. Leakage in the evaporation ponds can be measured by electrical conductivity and the concentration of salts which can quickly detect any leak (Ahmed et al., 2001), consequently the installation of pond liners is crucial to prevent further soil and groundwater contamination, (Ladewig and Asquith, 2012), which incurs considerable cost (Nicot et al., 2009)

Considering the parity between natural evaporation and traditional salt works, there is a strong argument to adopt an integrated approach for the solution of brine disposal management from thermal desalination plants. Therefore, this chapter aims to support the use of evaporation ponds as opposed to traditional salt works, to recover minerals and NaCl (halite) from brine, with particular reference to ZWPD in Libya, located on the southern Mediterranean coast. The work will also pave the way for further development of mineral salt exploitation from the brine disposed from thermal distillation plants.

7.1.1. Crystallisation of sodium chloride (Halite) in the saltern ponds

When saline water evaporates, it produces a sequence of salt formation, the first being calcium carbonate (calcium aragonite) at a concentration of 100-120 gl^{-1}

followed by calcium sulphate (gypsum) at concentration of 180 gl^{-1} and finally sodium chloride (halite) at salt concentration of 300–350 gl^{-1}, resulting in a concentrated mixture of magnesium, potassium, chloride and sulphate ions. The gypsum gathers at the bottom of the pond where the halite forms crystals (Madkour and Gaballah, 2012; Oren et al., 2009). These ponds operate continuously and seasonally, both maintaining a constant salinity gradient during ongoing production of salt, which is produced annually by the former and only during the summer by the latter (Davis, 2000).

7.2. Study Site and Evaporation Ponds Installation

An experiment was carried out in July 2014 to construct ten evaporation ponds next to the outlet of the Zwuarah distillation plant. These ponds are located in the north-western side of the city of Tripoli (Latitude 32°53'420" N and longitude 12°10'578" E) (**fig 7.1)**. They are shaped as irregular rectangles with dimensions of (5m) width, (4.5m) long and (0.25m) deep.

Prior to installation, the pond site was cleaned up to clear away gravel and coarse sand to prepare a top layer of clean sand. 21,000 tons of dry and soft clay sand were settled and compacted at site by a wheel loader. Banks around the perimeter of the evaporation ponds were built using concrete bound blocks. Dry white soft sea sand was equalised and compacted by using a skid steer loader in each pond. Ten black pond liners of high density polyethylene measuring approximately 6 × 7m with 0.5mm thickness were installed in the top layer of the lined ponds, welded together by adhesive liquid.

Following their installation, the outer areas of each pond were covered by concrete block and soil in order to prevent movement of the pond liners. The main objective of choosing these durable UV-resistant black pond liners is to enhance evaporation by absorption of solar radiation and to avoid any environmental issues. A Davis wireless vantage pro 2 weather station with data logger was installed next to the site in order to study the weather and weather patterns. The total area of all the evaporation ponds is about ($225m^2$). The depth of the brine in each pond was approximately (0.07-0.1m). A volume of 15.75 m^3 of brine from the evaporator of ZWDP for ponds was used to carry out the experiments.

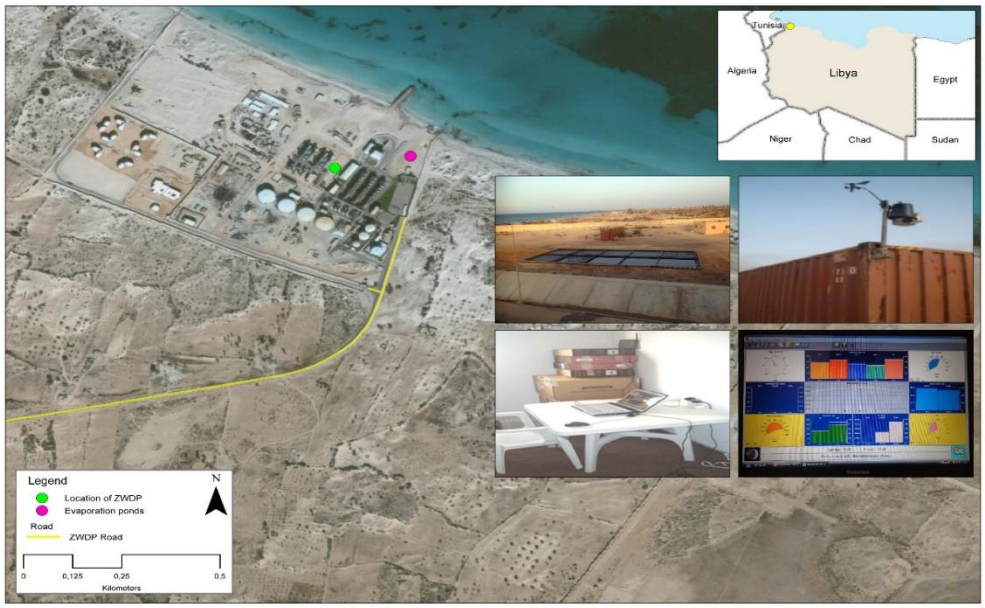


Figure 7. 1: Site of study (Google earth, 2016)

7.3. Sampling and Data Collection

The bulk element concentrations of chloride (mgl^{-1}), calcium (mgl^{-1}), magnesium (mgl^{-1}), sodium (mgl^{-1}), potassium (mgl^{-1}), sulphate (mgl^{-1}) and salinity (mgl^{-1}) were analysed in the Lab of ZWDP using Hach methods 2013 for water, wastewater and seawater and the mass of these elements (gr) was calculated for the brine sample collected from the evaporator of ZWDP. In addition, five brine samples were collected from the evaporation ponds and analysed up to the salt crystallisation stage (Halite) over five weeks at different salinity percentages (%).

Additionally, the weight percentages (%) of element concentrations were calculated (**Table 7.1**) to be compared with the quantified results obtained from scanning electron microscopy equipped with energy dispersive X-ray analysis (SEM-EDX) which allows only quantitative determination of the total soluble salt content in the salt crystal (Halite). The percentage of Halite (NaCl) purity and moisture was also determined and the total salt harvested (**fig 7.2)** from the ponds was weighed (**see appendix 7)**.

Table 7. 1: The bulk element concentrations (mgl-1) and the weight percentages (%) of list valuable elements in rejected brine up to the salt harvested NaCl stage at different salinity level.

Observation period	Sample source	Parameters						
	Brine of ZWDP	Cl^- (mgl^{-1})	Ca^{2+}(mgl^{-1})	Mg^{2+}(mgl^{-1})	Na^+ (mgl^{-1})	K^+(mgl^{-1})	$SO4^{2-}$(mgl^{-1})	Salinity (mgl^{-1})
		28,784	657	2,153	12,870	561	8,500	52,000
		Cl^- (gr)	Ca^{2+}(gr)	Mg^{2+} (gr)	Na^+ (gr)	K^+ (gr)	$SO4^{2-}$ (gr)	Salinity (%)
		2.90	0.07	0.22	1.30	0.06	0.85	5.2%
No. Weeks	**Brine of Evaporation ponds**	Cl^- (mgl^{-1})	Ca^{2+}(mgl^{-1})	Mg^{2+} (mgl^{-1})	Na^+ (mgl^{-1})	K^+(mgl^{-1})	$SO4^{2-}$(mgl^{-1})	Salinity (mgl^{-1})
End of 1st week		42,600	300	2,500	15,870	652	3,700	76,959
End of 2nd week		53,600	400	3,700	20,220	792	5,100	96,831
End of 3rd week		106,500	600	9,800	71,580	2660	10,300	192,389
End of 4th week		213,300	1200	28400	82500	7040	85100	385,337
Completely Evaporated at the end of 5th week (Salt)		5,006	39	176	637	2	116	9,043
No. Weeks	**Weight (gr)**	Cl- (gr)	Ca^{2+}(gr)	Mg^{2+}(gr)	Na^+ (gr)	K^+ (gr)	$SO4^{2-}$ (gr)	
End of 1st week		4.26	0.03	0.25	1.59	0.07	0.37	
End of 2nd week		5.36	0.04	0.37	2	0.08	0.51	
End of 3rd week		10.65	0.06	0.98	7.15	0.27	1.03	
End of 4th week		21.33	0.12	2.48	18.98	0.7	8.51	
Completely Evaporated at the end of 5th week (Salt)		0.5	0	0.02	0.32	0	0.01	
No. Weeks	**Weight (%)**	Cl- (%)	Ca^{2+}(%)	Mg^{2+}(%)	Na^+ (%)	K^+ (%)	$SO4^{2-}$ (%)	Salinity (%)
End of 1st week		4.26	0.03	0.25	1.59	0.07	0.37	7.7
End of 2nd week		5.36	0.25	0.37	2.02	0.08	0.51	9.7
End of 3rd week		10.65	1.59	0.98	7.16	0.27	1.03	19.2
End of 4th week		21.23	0.07	2.84	18.98	0.7	8.51	38.5
Completely Evaporated at the end of 5th week (Salt)		0.50	0	0.02	0.32	0	0.01	0.9
Salt harvested	**(NaCl)**	**NaCl Purity (%)**		**NaCl Moisture (%)**		**Extracted quantity from ponds (Kg)**		
		80.73		**0.52**		**309**		

Figure 7. 2: Salt harvested from the evaporation ponds at ZWDP

7.3.1. SEM and EDX Analysis (Salt Crystal Sample)

Samples of dried salt crystals were attached to aluminium studs with carbon glue to a sputter coated with gold to overcome the problem of charging during scanning electron microscopy SEM analysis. It is essential to provide the optimum contact for electrons across the surface of the sample through careful mounting and gold coating. The stud was loaded into an FEI Inspect SEM with an Oxford Instrument INCA analysis system. Conditions were 10kV; magnified at 43x, 117x and 154x with image scale 2mm, 1mm and 500µm respectively to determine salt shape (fig 7.3). Additionally, LEAD compound siedentopf Microscope with digital camera was used to visualise the salt crystals.

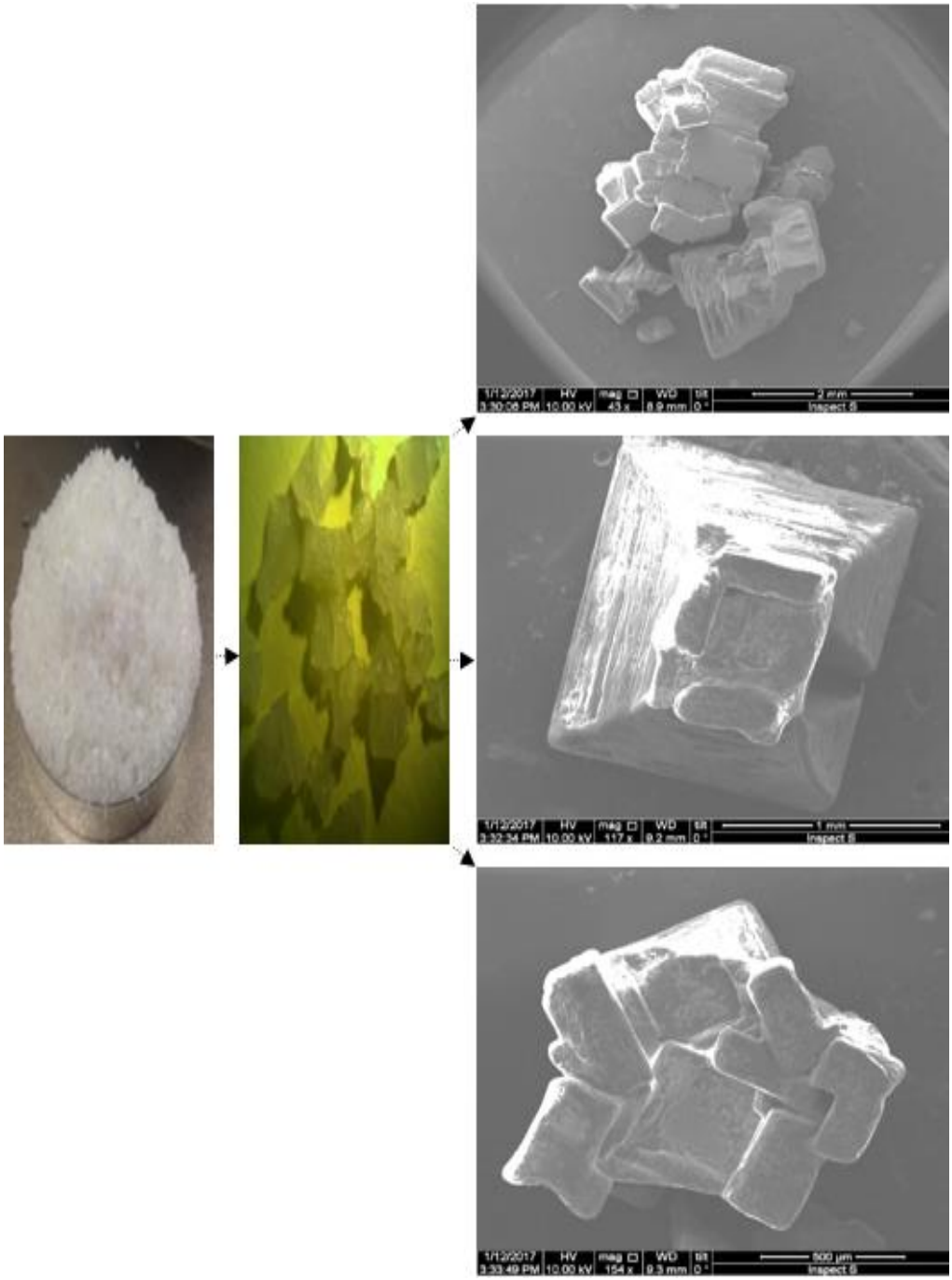


Figure 7. 3: Salt sample and SEM micrographs of NaCl crystals

The weight percentages (wt%) of chemical elements in the salt sample were carried out by energy dispersion of X-Ray spectroscopy (EDX) coupled with scanning electron microscopy (SEM) analysis. The salt sample was uncoated to remove the gold from the results and 20 kV voltages were used at image scale 1mm with magnification 117x. Data was processed with Sem Quant Software to identify and quantify the elemental constituents of the salt sample and five essential chemical elements were found in the salt sample (**Table 7.2**).

Table 7. 2: Essential chemical elements in salt sample

Element	Weight%	Atomic%
Oxygen	28.22	39.30
Sodium	41.38	40.10
Magnesium	5.06	4.64
Silicon	0.28	0.22
Chlorine	25.05	15.74
Totals	**100**	

7.3.2. Meteorological Data Collection

The Meteorological data was recorded over five weeks intervals between the months of August and September in the year 2014 using Davis Vantage Pro2 weather station from which subsequent daily averages were derived. The meteorological data includes the daily average air temperature (°C), relative humidity (%), wind speed (ms^{-1}) and direction, air pressure (KPa), solar radiation (Wm^{-2}), and precipitation (mm). All the data is presented in **Table 7.3** to estimate the evaporation rate at the site of study.

Table 7. 3: Meteorological data at site of study

Weeks	Date	Daily average high temperature (°C)	Daily average low temperature (°C)	Daily average humidity (%)	Daily average high Wind Speed (ms^{-1})	Daily average low Wind Speed (ms^{-1})	Wind direction	Daily average air pressure (kPa)	Daily average solar radiation (Wm^{-2})	Daily average rain (mm)
	05/08/2014	27.3	27.1	84.7	23.6	18.2	NNE	101.3	283	0
	06/08/2014	27.2	27.0	82.7	26.3	20.7	NNE	101.3	300	0
	07/08/2014	26.3	26.1	77.3	23.9	17.7	NNE	101.5	319	0
1st	08/08/2014	26.0	25.7	79.6	21.6	14.7	ENE	101.6	310	0
	09/08/2014	26.7	26.6	82.1	29.0	19.6	NNE	101.5	292	0
	10/08/2014	27.2	27.0	83.5	31.3	20.4	NNE	101.5	285	0
	11/08/2014	27.2	27.0	82.3	22.5	14.2	NE	101.5	302	0
	12/08/2014	27.6	27.4	76.8	15.7	10.3	ENE	101.4	299	0
	13/08/2014	27.9	27.6	70.0	15.1	9.8	NNE	101.2	295	0
2nd	14/08/2014	28.9	28.5	66.1	15.1	9.9	N	101.3	288	0
	15/08/2014	27.4	27.2	86.9	20.0	15.3	NNW	101.6	279	0
	16/08/2014	27.2	27.0	85.5	20.1	14.3	NNW	101.6	264	0
	17/08/2014	27.4	27.2	83.5	31.7	23.0	NNE	101.7	228	0

	18/08/2014	27.4	27.2	82.8	26.3	18.1	ENE	101.6	228	0
	19/08/2014	28.3	28.1	82.8	17.4	10.6	ESE	101.3	207	0
	20/08/2014	29.4	29.0	71.9	15.4	9.0	ESE	101.3	278	0
	21/08/2014	29.4	29.1	69.6	12.5	7.1	ENE	101.3	267	0
3rd	22/08/2014	29.9	29.5	58.6	13.9	8.3	E	101.4	262	0
	23/08/2014	29.7	29.3	65.6	13.4	8.2	NNE	101.4	287	0
	24/08/2014	27.9	27.7	85.7	24.6	18.6	NNE	101.6	281	0
	25/08/2014	27.3	27.1	80.6	22.3	16.0	NNE	101.8	270	0
	26/08/2014	27.6	27.4	80.6	21.6	14.2	ENE	101.6	269	0
	27/08/2014	28.4	28.1	77.8	18.7	13.0	N	101.3	270	0
	28/08/2014	27.9	27.7	83.1	26.2	20.3	N	101.4	274	0
4th	29/08/2014	27.5	27.3	83.4	17.2	12.4	NE	101.6	276	0
	30/08/2014	27.0	26.7	80.9	16.1	11.3	ENE	101.6	273	0
	31/08/2014	26.1	25.8	81.8	15.3	9.6	ESE	101.5	264	0
	01/09/2014	28.3	27.8	75.8	19.7	12.7	NNE	101.2	256	0
	02/09/2014	27.3	27.0	71.0	21.0	15.0	E	101.2	262	0
	03/09/2014	25.9	25.5	69.7	16.1	11.3	E	101.3	267	0
	04/09/2014	27.1	26.8	74.3	20.7	12.3	NE	101.3	257	0
5th	05/09/2014	27.7	27.5	83.1	23.7	15.2	NE	101.3	251	0
	06/09/2014	27.6	27.4	75.9	25.2	17.8	ENE	101.3	250	0
	07/09/2014	27.8	27.6	76.6	22.4	13.9	NE	101.3	256	0
	08/09/2014	27.1	26.8	74.3	20.7	12.3	NE	101.3	257	0

7.4. Estimation of Evaporation Rate at Site of Study

There are several techniques used to calculate evaporation rates, the most common being the use of an evaporation pan (Class A pan) (Ahmed et al., 2000). In this study, the Penman (1948) equation normally used by hydrologists to calculate evaporation rates from open water sources, was used in this case to quantify the evaporation rates from the evaporation ponds at the site of study. The Penman formula is written thus (Akridge 2008):

$$\lambda E = \frac{\Delta}{\Delta+\gamma} R_n + \frac{\gamma}{\Delta+\gamma} f(u)(es - e) \quad \text{(7.1)}$$

Where λ is the latent heat of vaporization (MJkg^{-1}), E is the evaporation rate expressed as (mmday^{-1}), Δ is the slope of the saturation vapour pressure curve (kPa °C^{-1}), γ is the psychrometric constant (KPa), R_n is the net solar radiation (MJ m^{-2} day^{-1}), $f(u)$ is wind speed (ms^{-1}) function, es and e are the saturation vapour pressure of water and ambient water vapour pressure, respectively (kPa). The aerodynamic parameters of Penman formula were estimated using standard equations as recommended by (Shuttleworth, 1993; Allen et al, 1998; Shuttleworth, 2007; Akridge, 2008).

The latent heat of evaporation λ (MJkg^{-1}) ranges in temperature and is determined by the following equation:

$$\lambda = (2.501 - 0.002361T) \quad \textbf{(7.2)}$$

Where T is represented in degrees celsius, it is the average of the daily maximum and minimum temperatures recorded at the site calculated thus:

$$T = \frac{T_{\max} + T_{\min}}{2} \quad \textbf{(7.3)}$$

The slope of saturation vapour pressure Δ (kPa °C^{-1}) is a function of temperature and can be calculated as follows:

$$\Delta = \frac{4098_{es}}{(237.3 + T)^2} \quad \textbf{(7.4)}$$

Where es (KPa) shows the pressure of saturation vapour, as calculated from daily average temperatures, it verifies the release of water molecules that are released from the liquid surface, calculated as follows:

$$e_s = 0.6108e^{\left(\frac{17.27T}{237.3+T}\right)} \quad \textbf{(7.5)}$$

The psychrometric constant (kPa °C^{-1}) can be identified as the following:

$$\gamma = 0.000655P \quad \textbf{(7.6)}$$

Where P is the atmospheric pressure (kPa) recorded by the weather station at the site.

At ground surface level, the parity between total upward and downward radiation fluxes is measured to give net radiation (R_n), which ultimately energises the processes of evaporation, evapotranspiration, air and soil fluxes (Imak et al., 2003). It can be calculated using a range of methods including direct measurement with a radiometer, analysis of Earth's orbital characteristics and published latitude tables (Akridge, 2008) which investigate monthly average net radiation rates (e.g. in Boxwell, 2016). Daily average net radiation was measured using the following equation:

$$Rn = 0.0864Q \quad \textbf{(7.7)}$$

Where Q is daily average solar radiation (Wm^{-2}).

Wind speed for an open water surface is calculated by the following formula:

$$f\ (U) = 6.43\ (1 + \ 0.536\ U_2)$$……...……...…...…….……. (**7.8**)

Where U_2 is the average of the daily maximum and minimum wind speed (ms^{-1}) recorded at 5.5 m above the surface at the site of study and is calculated thus:

$$U_2 = \frac{U_{\max} + U_{min}}{2}$$ ……...……..…....…….…… (**7.9**)

The vapour pressure e (KPa) can be determined from the relative humidity by the following equation:-

$$e\ = \frac{H_r e_s}{100}$$ ……..……...…….…….…….. (**7.10**)

Where H_r is the daily average of the relative humidity (%) recorded at the site of study by the weather station.

The estimation of the daily average evaporation rates from 5th of August to 8th September 2014 at the study site are presented in (**Table 7.4)**.

Table 7. 4: Daily average evaporation rates at the study site

Weeks	Date	Daily average temperature T (°C)	Daily average wind speed U_2 (ms^{-1})	Daily average latent heat of evaporation (λ) ($MJkg^{-1}$)	Daily average saturation vapor pressure (es) (KPa)	Daily average **slope** of saturation vapor pressure (Δ) (kPa °C^{-1})	Daily average Psychrometric constant (γ) (kPa °C^{-1})	Daily average net radiation R_n (MJ m^{-2} day^{-1})	Daily average wind speed function f (u) (ms^{-1})	Daily average vapor pressure (e) (KPa)	Daily average difference pressure (es-e) (KPa)	Daily average evaporation rate ($mmday^{-1}$)
	05/08/2014	27.15	20.89	2.44	3.60	0.21	0.07	24.45	78.44	3.05	0.55	11.88
	06/08/2014	27.10	23.50	2.44	3.59	0.21	0.07	25.89	87.42	2.97	0.62	13.41
	07/08/2014	26.20	20.80	2.44	3.40	0.20	0.07	27.52	78.12	2.63	0.77	14.63
1st	08/08/2014	25.85	18.15	2.44	3.33	0.20	0.07	26.76	68.98	2.65	0.68	13.05
	09/08/2014	26.65	24.28	2.44	3.49	0.21	0.07	25.26	90.11	2.87	0.63	13.48
	10/08/2014	27.10	25.85	2.44	3.59	0.21	0.07	24.62	95.52	2.99	0.59	13.25
	11/08/2014	27.10	18.37	2.44	3.59	0.21	0.07	26.06	69.72	2.95	0.63	12.49
	12/08/2014	27.50	13.00	2.44	3.67	0.21	0.07	25.85	51.23	2.82	0.85	12.34
	13/08/2014	27.75	12.47	2.44	3.73	0.22	0.07	25.52	49.39	2.61	1.12	13.33
	14/08/2014	28.70	12.51	2.43	3.94	0.23	0.07	24.86	49.54	2.60	1.33	14.04
2nd	15/08/2014	27.30	17.63	2.44	3.63	0.21	0.07	24.14	67.17	3.15	0.48	10.67
	16/08/2014	27.10	17.21	2.44	3.59	0.21	0.07	22.77	65.76	3.07	0.52	10.47
	17/08/2014	27.30	27.34	2.44	3.63	0.21	0.07	19.69	100.64	3.03	0.60	12.06
	18/08/2014	27.30	22.21	2.44	3.63	0.21	0.07	19.69	82.98	3.00	0.62	11.22
	19/08/2014	28.20	13.98	2.43	3.82	0.22	0.07	17.90	54.61	3.17	0.66	9.06
	20/08/2014	29.20	12.22	2.43	4.05	0.23	0.07	24.01	48.53	2.91	1.14	12.71
	21/08/2014	29.25	9.79	2.43	4.06	0.23	0.07	23.09	40.17	2.83	1.24	11.90
3rd	22/08/2014	29.70	11.10	2.43	4.17	0.24	0.07	22.63	44.69	2.44	1.73	14.17
	23/08/2014	29.50	10.81	2.43	4.12	0.24	0.07	24.82	43.67	2.70	1.42	13.55
	24/08/2014	27.80	21.60	2.44	3.74	0.22	0.07	24.29	80.87	3.20	0.53	11.79
	25/08/2014	27.20	19.16	2.44	3.61	0.21	0.07	23.30	72.45	2.91	0.70	12.26
	26/08/2014	27.50	17.89	2.44	3.67	0.21	0.07	23.25	68.07	2.96	0.71	12.00
	27/08/2014	28.25	15.83	2.43	3.84	0.22	0.07	23.34	60.99	2.98	0.85	12.28
	28/08/2014	27.80	23.25	2.44	3.74	0.22	0.07	23.68	86.55	3.10	0.63	12.69
4th	29/08/2014	27.40	14.79	2.44	3.65	0.21	0.07	23.88	57.40	3.04	0.61	10.86
	30/08/2014	26.85	13.72	2.44	3.53	0.21	0.07	23.60	53.72	2.86	0.68	10.94
	31/08/2014	25.95	12.47	2.44	3.35	0.20	0.07	22.83	49.41	2.74	0.61	10.11
	01/09/2014	28.05	16.20	2.43	3.79	0.22	0.07	22.09	62.25	2.87	0.92	12.39
	02/09/2014	27.15	17.98	2.44	3.60	0.21	0.07	22.65	68.38	2.55	1.04	14.08
	03/09/2014	25.70	13.68	2.44	3.30	0.20	0.07	23.11	53.58	2.30	1.00	12.64
	04/09/2014	26.95	16.51	2.44	3.55	0.21	0.07	22.20	63.31	2.64	0.91	12.64
5th	05/09/2014	27.60	19.47	2.44	3.69	0.22	0.07	21.71	73.52	3.07	0.62	11.25
	06/09/2014	27.50	21.51	2.44	3.67	0.21	0.07	21.57	80.56	2.79	0.88	13.67
	07/09/2014	27.70	18.15	2.44	3.71	0.22	0.07	22.11	68.98	2.85	0.87	12.72
	08/09/2014	26.95	16.52	2.44	3.55	0.21	0.07	22.20	63.35	2.64	0.91	12.64

7.5. Pond Surface Area and Depth Required for ZWDP

The design of a fully functioning evaporation pond is based on accurate evaporation data that needs to be carefully measured and recorded. The surface area required depends on volumes of brine disposal and evaporation rates. (Ladewig and Asquith, 2012). Optimum parameters of pond open surface area (A), minimum pond depth (D) recommended in design, and maintenance of evaporation ponds by (Ahmed et al., 2000) can be estimated from the following equations.

$$A = \frac{V * F_1}{0.7 * E_{ave}} \quad \text{(7.11)}$$

$$d_{min} = (0.2 + E_{ave}) * F_2 \quad \text{(7.12)}$$

Where A is the open surface area of the pond (m^2), V is the volume of reject brine (m^3/day), F_1 is an empirical safety factor to allow for lower than average evaporation rates, 0.7 is the value in the area in the equation representing the evaporation ratio. E_{ave} is the evaporation rate (m/day). d_{min} is the minimum depth (m), the value of 0.2m in depth equation is the freeboard for rainfall intensity, F_2 is a factor that incorporates the length of the winter season. ZWDP produces around 40,000 (m^3/day) of effluent to the marine environment of which 26,666.7 (m^3/day)is brine water, so the pond area and depth needed for ZWDP are estimated for low and high evaporation rates in (**Table 7.5)**.

Table 7. 5: Pond surface area and depth needed for ZWDP

Evaporation rates data (m/day)	F_1:Safety factor evaporation rate (m/day)	F_2: length of the winter season (days)	Volume of reject brine (m^3/day)	Surface Area required (m^2)	Depth (m)
Low : 0.009	0.0045	90	26,666.70	19,047.60	1.02
High : 0.015	0.0073	90	26,666.70	19,047.60	1.52

7.6. Cost Estimation of Evaporation Ponds Installation in Libya

The cost of installation of evaporation ponds in Libya was determined from communication with three Libyan local companies, namely Almsar El-Kabeer Ltd, Altbain Ltd and Alrqhobh ltd. The feasibility estimation of installing the evaporation ponds has been set out in a schedule of works with relevant details including site location (Latitude 32°53’40” N and longitude 12°10'40.3” E) in the north west of

ZWDP and land cost. The total area proposed for implementation of the project was **300,004 hectares**, divided into six evaporation ponds, each of which has a length of 1000 m and a 500 m width. Other factors for cost consideration include site clearing and preparation, earthworks incorporating outlying areas, building banks, installation of a pipeline system, pond liners, road and access, lighting systems and installation of a weather station. The project was designed to convey the brine disposed from ZWDP and seawater to the evaporation ponds (**fig 7.4**).

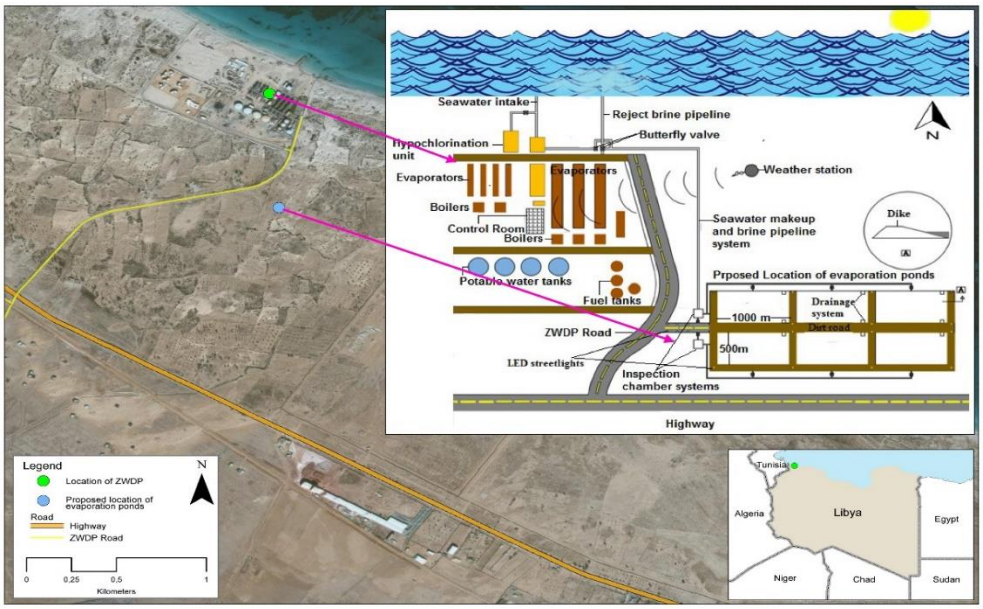


Figure 7. 4: Proposed project of evaporation ponds to estimate the total cost (Google earth, 2016)

This has been put out to tender to local companies in Libya who have submitted their prices to estimate the actual cost per hectare to build evaporation ponds (**Table 7.6**). These figures were assessed against Mickley equations used to calculate the cost of utilizing evaporation ponds for desalination plants that are valid from a range of 4.04686 to 40.4686 hectares.

Table 7. 6: Estimated cost of hectare to build evaporation ponds

Cost factors	Almsar El-Kabeer Ltd [$/ha USA]	Altbain Ltd [$/ha USA]	Alrqhobh ltd [$/ha USA]
Land Cost	6,896.5	6,896.50	6,896.5
Site clearing and preparation	10,344.8	11,724.12	13,793.1
Earthworks	2,206.9	2,413.8	2,758.6
Pipeline system installation	110,344.8	128,965.5	134,827.59
Lining the pond	48,275.9	55,172.4	58,620.69

Site access	88,137.95	88,275.85	93,793.11
Lighting system installation	18,056.4	20,689.6	22,758.6
Weather station installation	689.7	827.6	1,034.5
Total cost	**284,953**	**314,965**	**334,483**

Mickley's formulas for the total capital cost is written thus (Mickley, 2006)

$$Total\ capital\ cost\ (\$) = A_t \times CC_U \quad \text{..... (7.13)}$$

Where A_t is total area required (acres) and can be calculated from the following formula.

$$A_t\ (plus\ a\ 20\%\ of\ \ contingency\ factor) = (1.2A_e) \times \frac{1+0.155dh}{\sqrt{A_e}} \quad \text{..... (7.14)}$$

Where A_e is evaporative area (surface area of the pond) (acres) and dh is dike height (ft).

The total unit area capital cost CC_U (\$/acre) can be calculated from the following equation.

$$CC_U = 5406 + 465t_l + 1.07lC + 0.931C_c + 217.5d\text{h} \quad \text{..... (7.15)}$$

Where t_l is the liner thickness (mils), lC is the land cost (\$/acre), C_c is the land clearing cost (\$/acre).

Land cost between the three tenders is constant but there were differences between the three tenders in the estimated cost of land clearing and preparation. Hence, averages between the three companies quotes have been calculated in order to estimate the total capital cost of constructing 2.5 acres (1 ha) of evaporation ponds by using Mickley's equation (**Table 7.7**).

Table 7. 7: Capital cost of installation of evaporation ponds by mickley's equation

Factors	**Dimensions and costs**	**Unit**	**Total area (A_t) (acres) at 0.2 contingency factor**	**Total unit area capital Cost (CC_U) (\$/acre)**	**Total capital cost (\$)**
Surface area of the pond	2.47105	acres	**3.04**	**116, 163.3**	**353,136.4**
Dike height	3.93701	Ft			
Liner thickness	196.85	mils			
Land Cost	6,896.50	\$/acre			

Land clearing and preparation	11954.02	$/acre

7.7. Statistical Analysis

All the meteorological data include the daily average air temperature (°C), relative humidity (%), wind speed (ms^{-1}), air pressure (KPa), solar net radiation ($MJ\ m^{-2}\ day^{-1}$). Also included is the total weight percentages (wt%) for the ions composition of the five brine samples up to crystallisation stage collected from the evaporation ponds including Cl^{-} (mgl^{-1}), Ca^{2+} (mgl^{-1}), Mg^{2+} (mgl^{-1}), Na^{+} (mgl^{-1}), K^{+} (mgl^{-1}), $SO4^{2-}$ (mgl^{-1}) which were obtained from the field and lab work over the two months of the experiment. The results were transferred into PRIMER v6 software (Plymouth Routines In Multivariate Ecological Research version 6) (Clark and Gorley, 2006) in order to visualise the patterns of meteorological data which were collected daily and the total weight percentages (wt%) for ion compositions which were analysed at the end of each week over the study period. However, the daily average rainfall (mm) at the study site could not be included for statistical analysis, as it recorded nil during the period of study. All the data was normalised and then characterised by the principal component analysis (PCA) to generate 3D and 2D scatterplots displaying the distribution of the meteorological data and the ions composition of brine samples during the study period (**see appendix 7)**. A factorability of ±0.3 and greater was chosen because it is categorised as an important factor into each PCA (Williams et al., 2010; Pallant, 2010).

7.8. Results and Discussion

The aim of this work was to study the feasibility of salt production from reject brine released from distillation plants (MED plant) in the south Mediterranean on the western part of the Libyan coastline, using evaporation ponds. In order to obtain optimum evaporation rate results, black liners of high-density polyethylene were used, which ultimately resulted in the production of concentrated brine in a shorter time span, compared with traditional techniques. Information has been collated to provide a methodological process of using evaporation ponds as a means of brine management, described from technological, economical and environmental aspects.

At the study site, PCA analysis based on meteorological parameters resulted in five components (**fig 7.5**) and the pattern during the period of study is best explained in PC1 with 47.6% of the total variance. In addition, PC2, PC3, PC4 and PC5 accounted for 69.1%, 83.6%, 94.2% and 100% of the total variance respectively. The pattern between meteorological parameters in PC1 is best explained with average daily temperature (°C) (-0.48), humidity (%) (0.57), wind speed (ms^{-1}) (0.50), and air pressure (KPa) (0.44). In PC2 the pattern between the meteorological parameters is best explained with average daily temperature (°C) (0.3) and solar radiation (Wm^{-2}) (-0.93). In the PC3 the pattern between meteorological parameters is best explained with average daily temperature (°C) (0.35), wind speed (ms^{-1}) (-0.41), air pressure (KPa) (0.84). In the PC4 the pattern between meteorological parameters is best explained with average daily temperature (°C) (0.74), wind speed (ms^{-1}) (0.57) and solar radiation (Wm^{-2}) (0.34). In the PC5 the pattern between the meteorological parameters is best explained with humidity (%) (0.79), wind speed (ms^{-1}) (-0.47), and air pressure (KPa) (-0.31).

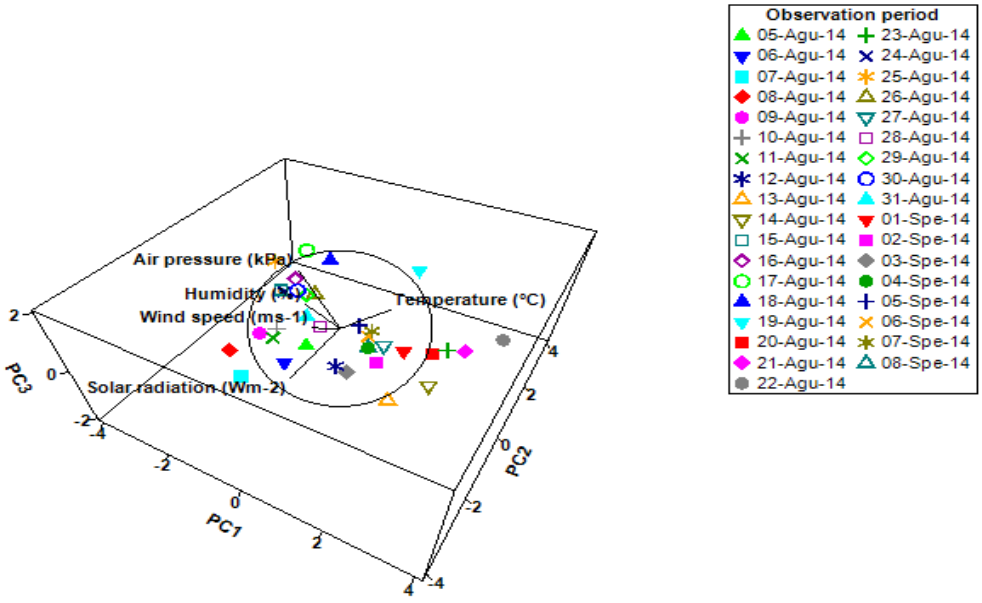


Figure 7. 5: 3D (PCA) ordination of meteorological parameters at the study site

Meteorological data (**Table 7.3**) over the period of study included daily average high and low temperatures (°C) (**fig 7.6** and **fig 7.7**), humidity (%) (**fig 7.8**), air pressure (kPa) (**fig 7.9**), daily average high and low wind speed (ms^{-1}) (**fig 7.10 and fig 7.11**), solar radiation (Wm^{-2}) (**fig 7.12**) and daily average evaporation rate ($mmday^{-1}$) (**fig 7.13**) at site of study indicating that the area is generally hot, dry and semi-arid.

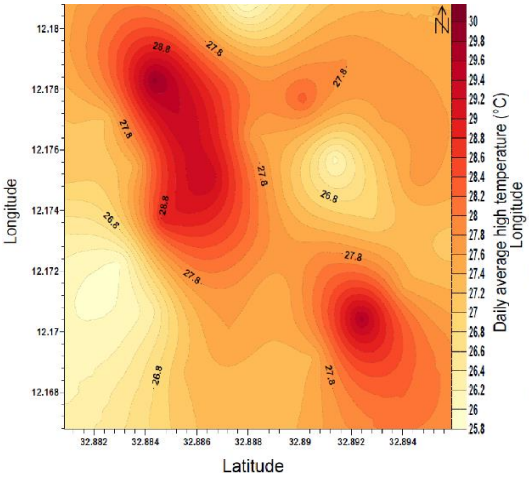


Figure 7. 6: High temperature (°C)

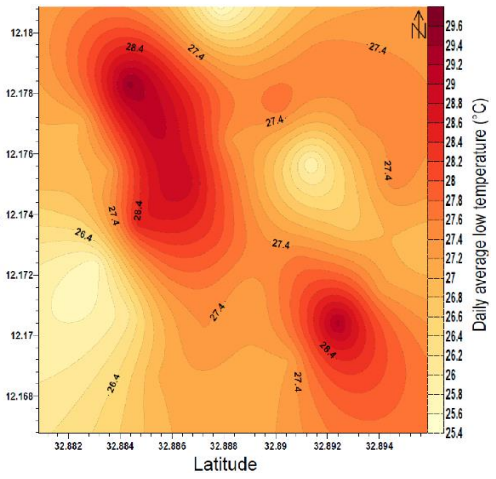


Figure 7. 7: Low temperature (°C)

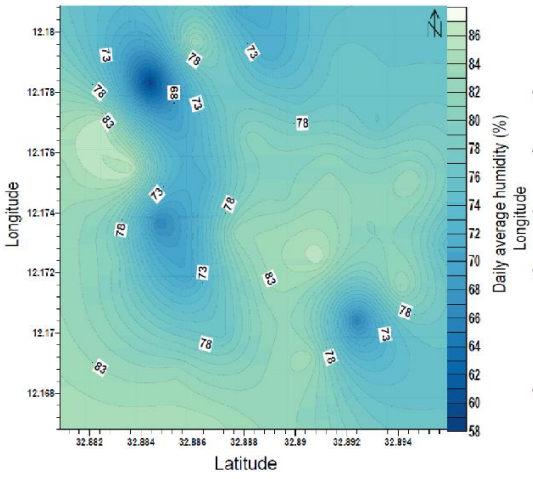


Figure 7. 8: Humidity (%)

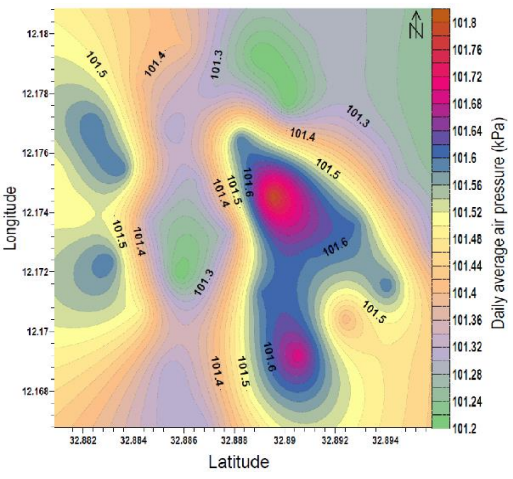


Figure 7. 9: Air pressure (kPa)

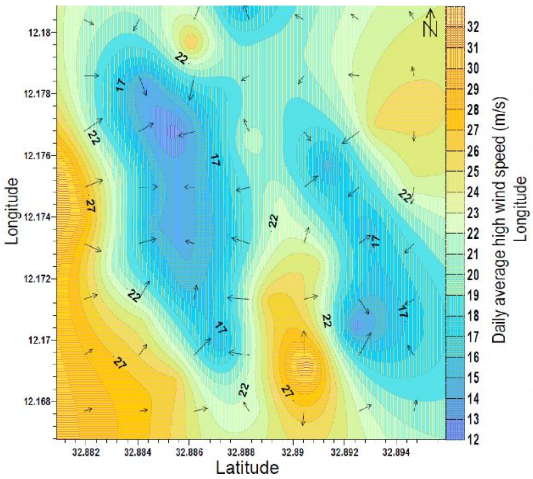


Figure 7. 10: High wind speed (ms^{-1})

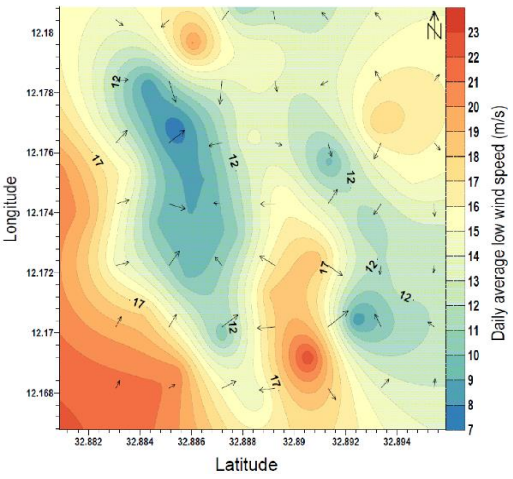


Figure 7. 11: Low wind speed (ms^{-1})

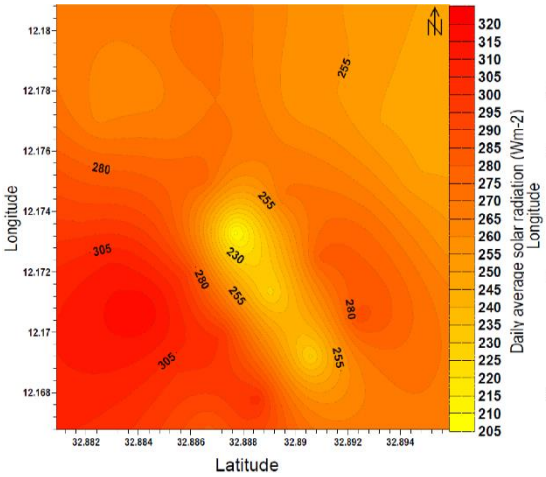


Figure 7. 12: Solar radiation (Wm^{-2})

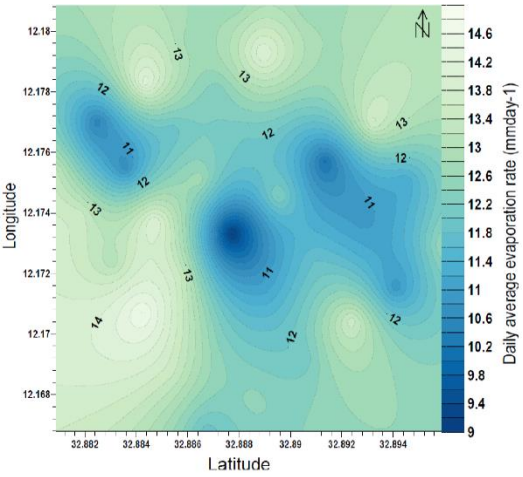


Figure 7. 13: Evaporation rate ($mmday^{-1}$)

The daily average high temperature fluctuated between 25.9°C and 29.9°C, while the daily average low temperature varied between 25.5°C and 29.5 °C. The daily average relative humidity ranged between 58.6% and 86.9%. There are intermittent wind regimes in the site of study where direction varied considerably, mainly from north-northeast (NNE), east-northeast (ENE), northeast (NE), north (N), north-northwest (NNW), east-northeast (ENE), east-southeast (ESE) and east (E) with daily average high wind speed alterations between 12.5 ms^{-1} and 31.7 ms^{-1}, while the daily average low wind speed ranged between 7.1 ms^{-1} and 23 ms^{-1}. The daily average air pressure varied between 101.2 (kPa) and 101.8 (kPa) and solar radiation from 207 Wm^{-2} to 319 Wm^{-2}. This contributed to the lowest daily evaporation rate occurring in August and found to be 9.06 $mmday^{-1}$ while the highest daily average evaporation rate occurred in September, found to be 14.63 $mmday^{-1}$. However, results were found by Benzaghat et al., 2011, who studied estimation of evaporation rates using the Penman method on the north coastline of Libya which ranged 4.1 to 12.1 mm/year with daily average 9 $mmday^{-1}$. The outcome of the daily average evaporation rates indicated that the evaporation is largely dependent on climate variables.

Final lab analysis also showed that useful end-products can be generated from the evaporation of the brine disposed from ZWD plant at different salinity levels. Major concentration of salts and minerals were found in brine including Cl^- , Ca^{2+}, Mg^{2+}, Na^+, K^+ and SO_4^{2-} and salt in the form of NaCl.

PCA analysis of the total weight percentages (wt%) for the ions composition of the five brine samples up to crystallisation stage resulted in four components (**fig 7.14**)

and the pattern during the period of study is best explained in PC1 with 82.1% of the total variance. In addition, PC2, PC3 and PC4 accounted for 99.8%, 100% and 100% of the total variance respectively. The pattern of the total weight percentages between ions composition in PC1 is best explained with Cl^- (wt %) (-0.445), Mg^{2+} (wt %) (-0.451), Na^+ (wt %) (-0.450), K^+ (wt %) (-0.450) and $SO4^{2-}$ (wt %) (-0.439). In PC2 the pattern of the total weight percentages between ions composition is best explained with Ca^{2+} (wt %) (-0.969). In PC3 the pattern of the total weight percentages between ions composition is best explained with Cl^- (wt %) (0.853), Na^+ (wt %) (-0.334) and $SO4^{2-}$ (wt %) (-0.348). The pattern of the total weight percentages of ions composition in PC4 is best explained with Mg^{2+} (wt %) (-0.406), Na^+ (wt %) (0.306), K^+ (wt %) (0.678) and $SO4^{2-}$ (wt %) (-0.507).

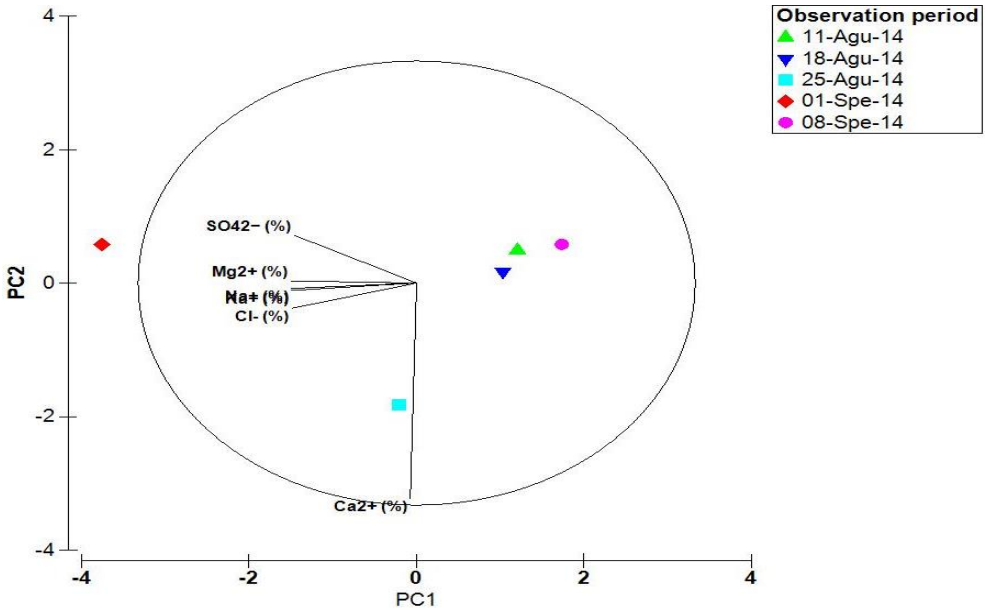


Figure 7. 14: 2D (PCA) ordination of metrological parameters at the study site

The outcomes of the total weight percentages (wt%) calculated from the concentrations of ions by titration using Hach methods for the brine and salt sampled during five weeks at different percentages of salinity level (**Table 7.1 above**) indicated that, the wt% of the salt is primarily influenced by Na^+ and Cl^- at the fifth week alongside other elements such as Mg^{2+} and $SO4^{2-}$. There was a significant increase in wt% of Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and $SO4^{2-}$ up to the fourth week, followed by a notable decrease in wt% in the fifth week. The observed variation can be attributed to the gypsum crystallisation at this stage which revealed fluctuations of salinity level. At salinity level 7.7%, the wt% of extracted chemical elements of Cl^-, Ca^{2+}, Mg^{2+},

Na^+, K^+ and $SO4^{2-}$ varied between 4.26%, 0.03%, 0.25%, 1.59%, 0.07% and 0.37% respectively, while at salinity level 9.7%, the wt% of extracted chemical elements of Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and $SO4^{2-}$ varied between 5.36%, 0.04%, 0.37%, 2.02%, 0.08% and 0.51% respectively, whereas at salinity level 19.2% the wt% of extracted chemical elements of Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and $SO4^{2-}$ varied between 10.65%, 0.06%, 0.98%, 7.15%, 0.27% and 1.03% respectively, while, at salinity level 38.5% the wt% of extracted chemical elements of Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and $SO4^{2-}$ varied between 21.33%, 0.12%, 2.48%, 18.98%, 0.7% and 8.51% respectively. At salinity level 0.9% the wt% of extracted chemical elements of Cl^-, Mg^{2+}, Na^+, and $SO4^{2-}$ varied between 0.5%, 0.02%, 0.32%, 0.01% respectively, however Ca^{2+} and K^+ did not exist at this level of salinity, which is possibly due to crystallisation of salt (NaCl) of a purity reaching 80.73% with moisture 0.52%. The results of the analysed brine samples from the evaporation pond showed considerable variation in the ions composition which may be attributed to high salinity levels due to intense evaporation taking place in the ponds that were not detected in the analysis.

SEM/EDS analysis was performed on the salt crystal samples to determine their crystallographic structure and to identify wt% of the chemical elements present in the salt crystal samples. The investigation results in (**Table 7.2, fig 7.3 above**) indicated that the EDS spectrum of the salt crystals sample exhibited two highly intense peaks of Na^+ and Cl^- at 41.38% and 25.05% of the total wt% respectively, in contrast with low intense peaks of Mg^{2+} and Si at 5.06% and 0.28% of the total wt% respectively. Meanwhile, O_2 represented only about 28.22% of the total wt% and the absence of other chemical elements shows that salt crystal samples have good purity with a homogeneous crystallographic structure (**fig 7.15)**. Addala et al., 2013 also supported the notion that the significant intensities of peaks indicate high crystalline quality. The crude salt produced from the evaporation ponds indicated a strong presence of Na^+ and Cl^- alongside other impurities present in small but significant quantities. This is in accordance with a study by Kasedde, (2013), who recorded an average proportion of halite (NaCl) in grade 1 as 92%, 64% in grade 2 and 65% in grade 3 for the salt production from salt works. Hence from the present investigation, the result of the mineralogical analysis of the salt by EDS analysis indicates that the crude salt yield from the evaporation ponds ranged between grade 1, 2 and 3 compared to conventional method of salt production. On the other side, that result indicates that the concentration

of toxic trace metals or elements in the salt harvested from the experimental study did not exist. Therefore, the outcome reveals that the NaCl produced from the brine disposed from distillation plants can be commercialised in the food and industrial sectors.

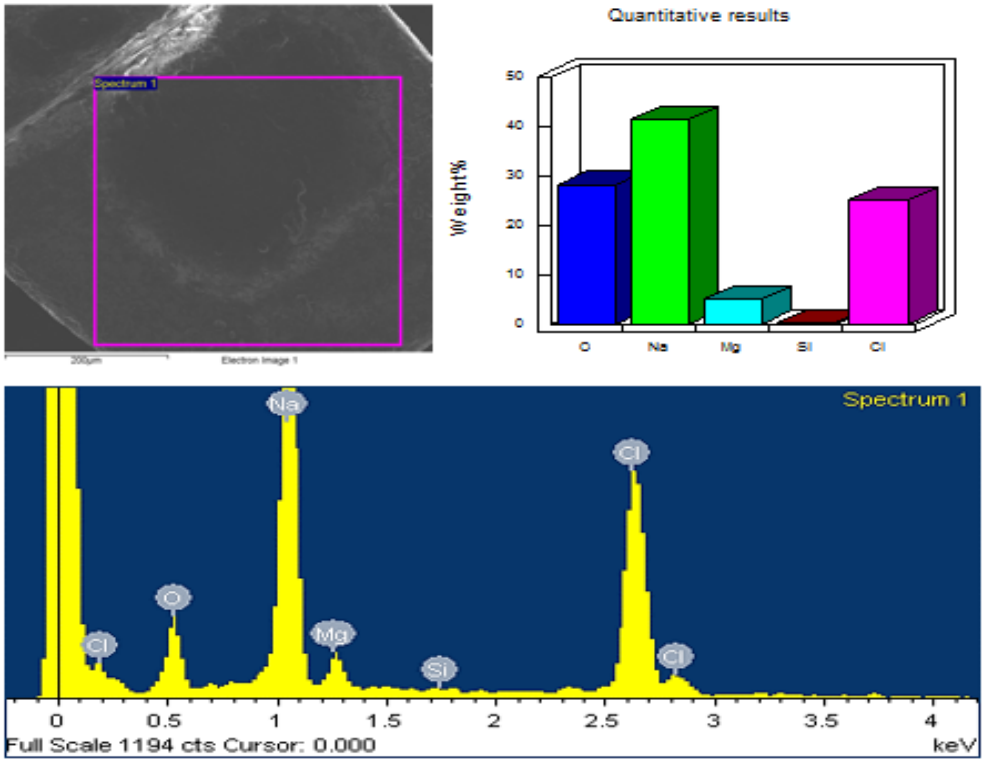


Figure 7. 15: EDX analysis of salt crystal harvested of evaporation ponds

The calculated pond surface area and depth required for ZWDP revealed that at low and high evaporation rates ranging between 0.009 and 0.05 m/day, the total surface area of evaporation pond to accumulate the brine disposed is roughly 19,047.60 m^2 with depth varying between 1.02 to 1.52 m. In addition, the outcomes of the experimental fieldwork in the evaporation ponds revealed that a volume of brine of 15.75 m^3 produces about 309 kg of salt within an area of 255m^2 and depth variance of 0.07-0.1m, thus demonstrating that by increasing the outlying area and the volume of brine, it is likely to instigate salt production. Consequently, as ZWDP disposed about 26,666.7 $m^3day^{-1}$of the brine, it is anticipated that about 523,175.261kgday^{-1} could be extracted in the form of salt.

The calculated total capital cost of constructing evaporation ponds by Mickley's equation was slightly higher $/ha 353,136.4 than the total capital costs estimated in

the quotes from Almsar El-Kabeer Ltd, Altbain Ltd and Alrqhobh Ltd at $/ha284,953, $/ha314,965, and $/ha334,483 respectively (**fig 7.16**), because 20% is assumed as a design contingency in the Mickley's equation.

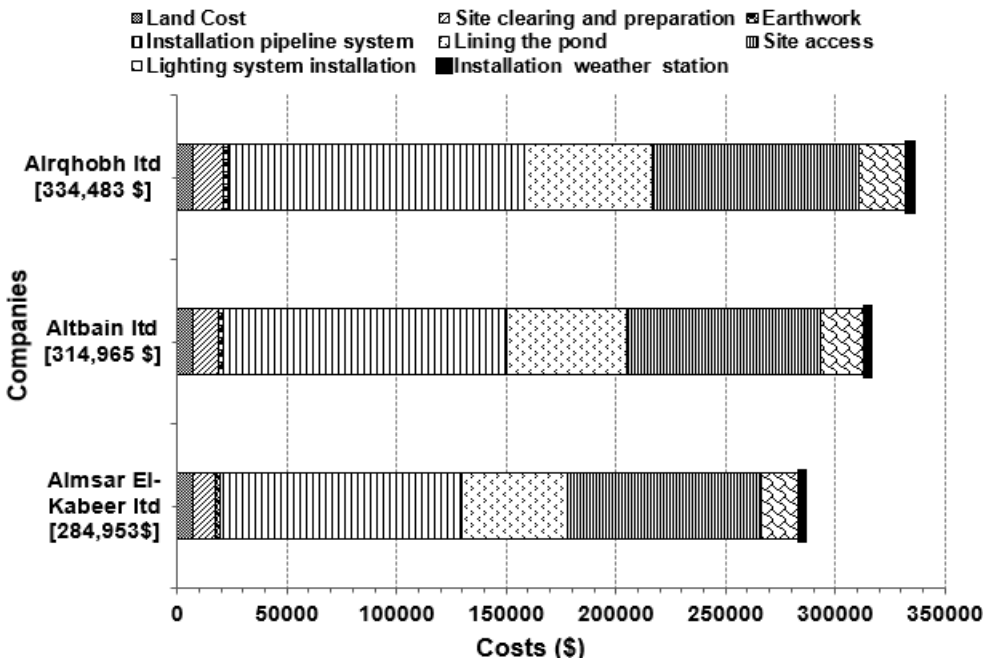


Figure 7. 16: Installation cost of one hectare of evaporation ponds by local companies.

The estimates proffered by the three companies do incorporate a contingency cost factor, but are not expressly identified as a percentage. The results also revealed that the cost factors of an evaporation pond including installation of a pipeline system, pond liner and site access constitute the highest expense, compared to other cost factors. These findings are in concordance with the results reported in literature concerning pond liners. The named companies claimed that the installation cost factors of constructing evaporation ponds, such as site access and lining the pond, can be reduced by using an alternative to synthetic materials, such as the finest grade of limestone powder produced from the white limestone quarries on the Libyan coastline for lining the pond and building roads. This option could reduce construction costs and the risk of contamination of subsoil and groundwater by hot brines, further improving evaporation rates at the site.

More than 30% of the total global production of sodium chloride (table salt) is derived from solar evaporation ponds (Ahmed et al., 2009). According to the prices obtained from leading industrial websites, such as (www.Alibaba.com) the current market price

for sea salt (sodium chloride) with a purity of 99% ranges between US $ 50-100/ tonne, and high quality food grade pool sodium chloride ranges between US $340-360. Another website (www.econmist.com) was also used to investigate the current market price of the lowest grade of gritting salt for de-icing roads. According to this website, the value of salt per tonne ranges between $ 40-50 in America and Britain. Another study by Abdulsalam et al., 2016 was also used to investigate the price of different minerals showing that the price of sodium and magnesium ranges between US $ 350 - US $ 2,410 respectively.

The recovery of such salt or minerals can generate significant revenues annually for Libya resulting in major investment across public and private sectors, particularly within the environmental and economic infrastructure. This is because the geographical location is eminently suitable for the evaporation ponds as it has a mild, dry temperature and high annual evaporation rates, combined with minimal land costs and availability.

The cost of land per hectare for the evaporation ponds can be offset against combinations of promoting synergies using aquaculture practices, such as the sale of *Artemia salina.* This does not occur in highly saline conditions, so in order to extract it, the salinity level in the ponds needs to be reduced and controlled by mixing brine with seawater, hence the total area designed to accumulate the brine from ZWDP was 300,004 hectares because its continuous daily brine disposal merits further investment. Therefore, by processing 9,733,345.5 (m^3/year) of reject brine disposed from ZWDP, it would be possible to produce commercial salts of NaCl worth 190,958,968.86 kg/year which is about US $ 9,547,948,442.86 annually, so this is the most sustainable and optimistic scenario.

In terms of full pond production planning, according to Butts (2011) the actual time needed to reach stabilisation always takes longer than scheduled. Original predicted time frames are invariably not met, due to factors such as pond conditioning as well as brine inventories. Aspects of brine exchange features are not adequately accounted for in the initial stages of the pond operation. In fact, even the most basic pond system such as NaCl production from ocean brine can take 3 to 4 years. The duration of the process could be 12 months for the brine to reach the required concentration and two

or three years more to lay down a floor. Consequently, salt production cannot commence until the fourth or even the fifth year.

7.9. Summary

According to experimental work in this chapter, this study has revealed that the best way to recover salt and minerals for domestic, commercial and industrial use, an integrated cycle that utilises a distillation plant with evaporation ponds is undoubtedly the best method, in terms of production, cost and efficacy, in contrast with more conventional salt extraction methods. Furthermore, the quality of the end-product shows a huge potential for further development and investment by building more desalination plants on the Libyan coastline.

From the short timescales involved to obtain salt or minerals, it would appear that the use of evaporation ponds is clearly effective in evaporating brine. The chemical and mathematical analysis data obtained by Hach methods from the brine samples collected indicated that the wt% of chemical compositions (Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and $SO4^{2-}$) and salinity levels continued to increase exponentially. In contrast, the wt% of Ca^{2+} decreased in the fourth week followed by a fall in the wt% of chemical compositions when reaching gypsum crystallisation stage (pure salt). Further to this, the wt% of Ca^{2+} and K^+ was non-existent when the brine evaporated in the form of salt. However, in the SEM/EDS test, halite (NaCl) was the main mineral evident during crystallisation of the salt samples, due to elevated surges of Na^+ and Cl^-. This proves the efficacy of evaporation ponds for the production of high quality products, at little or no environmental cost. It also paves the way for further investment and development of an eco-friendly venture that will ultimately propagate further economic growth for Libya, while providing further work opportunities. The next chapter will provide the conclusion and suggestions for future work of this thesis.

Chapter Eight: Summary and Conclusion

8.1. Introduction

The aim of this work was to determine the physico-chemical effects of brine influx from thermal desalination plants on the marine environment. Therefore, this chapter aims to present the overall summary and conclusion of the contribution of this research, in addition to providing limitations, recommendations, future work and validity of the research data collection and results.

8.2. Summary and conclusion of contribution

Over recent decades, several thermal and membrane water desalination processes have emerged and evolved in a bid to incorporate the best methods, taking economic and safeguarding factors into consideration. One such method that has been the focus of research is membrane desalination that includes design of the membrane module, energy recovery and pre-treatment methods as a cost-effective alternative to thermal processes such as MSF and MED. This is due to a lower demand for chemicals, improved operational and refining processes that reduce scaling, corrosion and anti-fouling. This membrane technology has also been found to be more cost effective for brackish water than seawater, due to low salinity. Conversely, larger-scale operations such as MED and SWRO tend to be more economical due to economy of scale and high efficiency in comparison to MSF. According to published literature on this topic, water costs vary based on different factors such as i) fuel cost, (ii) material and construction cost, (iii) feed water properties (salinity and turbidity), (iv) methods of cost calculation and desalination capacity. Gradually, thermal desalination such as MED and MSF for large-scale operations is gaining more momentum, particularly in arid and semi-arid regions where fuel sources are plentiful such as North Africa and the Middle East where distillation technologies are combined with power plants for optimum efficiency and economy. As CO_2 emissions escalate, there is need for alternative sustainable power sources such as solar power, but this is not feasible due to the need for large areas of land and higher operating costs. As seawater desalination techniques produce fresh water, there is concern about the by-products (brine) and its potential damage to the marine environment. During the desalination process, the use of

agents and chemicals to deal with the various stages of water treatment as well as salinity and thermal energy still remain a cause for concern in terms of environmental damage.

Presently, in literature there are no published legal regulations regarding the impacts of brine disposal across the Mediterranean. The current brine management strategies globally practised have provided some options for the treatment of brine disposed from desalination plants. Each scenario presents benefits and drawbacks, considering those that are not feasible such as direct discharge, discharge via wastewater treatment plants, discharge to the sewage systems, deep well injection, land application/spray irrigation and landfill disposal. None of these is viable because of environmental implications and poor economy of scale. One possible option was a co-charge of concentrate with power plant cooling water but when applied in coastal desalination areas, the salinity of the ambient receiving seawater will increase which will affect marine life. Other suggestions such as zero liquid discharge using crystallisers, wind aided intensified evaporation, dew evaporation, salt recovery salt solidification and sequestrations (SAL-PROC) and other brine management methods used for membrane techniques have proved impractical due to high energy demands and costs. Currently, such methods are used for small-scale operations and are still under development. Recently, one of the best options has been found to be the use of evaporation ponds in arid or semi-arid places which would be very cost-effective when coupled with aquaculture or salinity gradient solar ponds. However, in damp and humid conditions, this would not be feasible due to low evaporation rates.

In Libya, as water resources are rapidly being exhausted due to an increase in both population growth and water consumption in various sectors, the Libyan government has turned to integrating non-conventional water resources such as multi-effect distillation (MED and MED with TVC) to compensate for the water deficit. This research has determined that the cost of desalinated water by thermal desalination plants is about \$0.43/m^3, thus seeing this as the best option for providing water resources, due to unlimited seawater sources, compared with the cost per cubic metre produced by the Great Man-Made River Project, which is estimated to cost 0.83\$/m^3, Additionally, the water transferred during the two main

phases is about 4.5 million m^3day^{-1} while the rest of the phases are still under construction. Moreover, the results indicate that the highest annual water deficit in Libyan water regions was in Jabal Nafusah and Jifarah plain, Middle Zone, and Aljabal Alakhdar Region in the north and middle of the country equalling 1,450 million m^3, 250 million m^3, and 60 million m^3 respectively, while, there is surplus water in Fezzan, Alkufrah and Assarir region because those regions are supplied by Great Man-Made River tanks; additionally, most studies have indicated that the lower ground layers are rich in fresh water at those regions. From data analysis, the total numbers of desalination stations operating in Libya was estimated to be more than 20, with a total actual water production of 493,647 m^3day^{-1}. Most desalination plants are located on the coastline belt of the country; hence, the total brine disposal from those plants is estimated to be 329,098 m^3day^{-1}. Hence the results of case studies, of determining the impact of physico-chemical effects of brine influx from thermal desalination plants on the Libyan coastline, **as the main contribution within this research** revealed that, the brine disposal from both thermal desalination plants releases chemical residues and thermal energy which negatively affect the marine ecosystem. An increase in concentration of a number of ions and compounds from discharged brine indicates an alteration in the physico-chemical properties of the seawater. A significant positive correlation was observed at ZWDP and WTRIS between the biological data and physico-chemical parameters (r_s=0.673; p=0.002) and (r_s=0.637; p=0.003) which demonstrates the impact of brine disposal from both sites on the marine environment. Although at both sites, the brine was mixed with cooling water (seawater) before being disposed into the marine environment, it can be said that as result of continued brine discharge it is most likely to effect the surrounding environment. Additionally, there is an indication that it's likely that the desalination plants located on Libya coastline will cause future ocean acidity as result of CO_2 emissions because most of those plants run on heavy fuel.

The result obtained from the first sub contribution within the research revealed that, the brine can be recycled in the form of sodium hypochlorite (NaOCl). The laboratory experiment revealed that production of NaOCl for graphite electrodes (MCCA 1.82 gr/m^3) was significant. It showed high stability in performance, producing sodium hypochlorite to a value of approximately

2,600ppm. Furthermore, having a 4cm gap between electrodes with current density of 0.048 mA/cm was a crucial factor in terms of good process economy. Thus the cost of sodium hypochlorite yield of 2600 ppm at 24 kw/m^3 is expected to be 7.2 \$/m^3, which could be reduced by mixing the brine with the seawater to reduce the salinity level before utilizing it in the electrochemical cell. Hence, it can be concluded that brine has many favourable properties when considering the environmental and cost factors pertaining to coastal desalination plants in environmental and commercial terms. **While the second sub contribution within this research** revealed that, the brine can be recycled in the form NaCl, the investigation results indicated that the EDS spectrum of the salt crystals sample exhibited two highly intense peaks of Na+ and Cl^- at 41.38% and 25.05% of the total wt% respectively, in contrast with low intense peaks of Mg^{2+} and Si at 5.06% and 0.28% of the total wt% respectively. Meanwhile, O_2 represented only about 28.22% of the total wt% and the absence of other chemical elements shows that salt crystal samples have good purity and a homogeneous crystallographic structure. The result of calculating the evaporation rate revealed that the lowest daily evaporation rate occurred in August and was found to be 9.06 $mmday^{-1}$ while the highest daily average evaporation rate occurred in September, and was found to be 14.63 $mmday^{-1}$. The outcomes reveal that the NaCl produced from the brine disposed from distillation plants can be commercialised in the food and industrial sectors.

8.3. Limitations of research

There are often restrictions when doing PhD research due to limited resources or data, specific subject sources, or time and funding constraints (Sekaran and Bougie, 2009). When assessing existing water resources in Libya as a key factor within this research, there were very few up-to-date academic publications on the subject, or any type of formal reports written by Water Authorities. A further challenge was the fact that there had been no research previously completed to investigate the impact of brine influx from thermal desalination plants, especially on the Libyan coastline, which made it impossible to make valid comparisons on the physico-chemical effects in other regions on the Libyan coast, which is why comparisons have been made with results in other countries such as Spain etc. As the Libyan

coastline is covered by *Posidonia oceanica and Cymodocea nodosa* which has been classified as a healthy environment for marine species, the initial plan was to investigate and study the effects of varying brine salinity levels on these type of seagrasses. However, due to time restrictions and the situation in Libya affecting logistics, these factors have prevented extension of research. Therefore, this objective is presented for future work.

As the study of the brine impacts on the marine environment was carried out in May 2013, there are limits to the reliability of data due to seasonal difference. It is recommended that further study is conducted over different periods throughout the year.

8.4. Recommendations

Due to the ever increasing population growth, there will be a subsequent increase in the demand for water. Currently, water resources are constantly being depleted so it is important that measures are put in place to rectify this issue.

- It is recommended that an effective water-pricing system is established by Water Authorities across all sectors in a bid to conserve natural resources.

- Further wastewater treatment plants are required, to be installed by Water Authorities in order to continue the recycling of wastewater from sewage and the brine discharged from desalination plants to satisfy the growing demands across different sectors such as agriculture, industrial and commercial.

- It is advised that irrigation systems are improved and updated to control water usage with a robust policy in place to monitor usage.

As brine disposal is continually occurring along the coastline, particularly in arid and semi-arid regions such as Libya, where the technology is needed, there are growing environmental concerns. With raised salinity and temperatures and varying physico-chemical parameters of seawater, it is incumbent on the government to put measures in place for safe disposal options to protect marine ecosystems.

- In benthic areas and wetlands, the habitat is particularly vulnerable to the effects of brine influx, so Water Authorities should consider moving away from such protected areas.

- Annual reports are to be conducted by Water Authorities that scrutinise and monitor impacts of brine disposal, ultimately minimizing any potential hazards that threaten the marine ecosystem, with frequent consultation. Such reports need to include results of studies that measure the impact on marine species, carried out under a range of climatic conditions, measuring seasons and inter-annual differences.

- Closer liaison with the Environmental Authorities and General Desalination Companies in Libya is recommended to establish policies and service-level agreements that set out agreed operating standards and practices that can be replicated throughout the coastline areas. Studies are strongly encouraged into the use of concentrates and chemical compounds found in brine, and their results may warrant more conservative levels.

- Environmental Authorities are advised to collaborate with industrial, agricultural and commercial sectors as well as oil refineries regarding wastewater effluent management.

- All monitoring data is to be published and shared publicly, and made readily available on the internet at no cost.

- Ongoing government legislation on environment protection to be based on MAP-UNEP guidelines, with continuing liaison with specialists, conservationists and hydrologists in the field of desalination technology.

8.5. Future research

In order to capitalise on full exploitation of brine disposed from thermal desalination plants and to protect the marine environment, future work is planned pursuant to this research.

- There are beneficial seagrasses along the Libyan coastline such as *Posidonia oceanica and Cymodocea nodosa* which enable other marine life to reproduce and thrive. Therefore, further attention is required to study different salinity levels of brine and the long term impact on these types of seagrasses.

- As mentioned previously, sodium hypochlorite can be produced from recycled brine using electrolysis by graphite electrodes. The use of titanium electrode coated with a dimensionally stable anode (DSA) mesh using electrolysis warrants further research.

- Regarding the use of evaporation ponds on the Libyan coastline to recycle the brine disposed from thermal desalination plants in the form of minerals and salt, there is a need for further work to ascertain the optimum conditions of using solar energy for salt extraction. Once salt has been extracted from the evaporation ponds, there is scope for further study into the possibility of cultivating brine shrimp in the ponds at low salinity and temperature, which can be controlled by the seawater flow.

- Further research for longer periods of study during different seasons throughout the year is recommended to investigate the impact of brine on the marine ecosystems.

References

Abufayed. A and El-Ghuel. M. (2001) Desalination process applications in Libya, *Desalination*, [online], v.138 (3), September, pp.47-53
Available at: http://www.sciencedirect.com/science/article/pii/S0011916401002430
[Accessed 24th July 2014]

Al-Hengari. S, ElMoudir. W and El-Bousiffi. M. (2015) Economic assessment of thermal desalination processes, *Desalination and Water Treatment*, [online], v.55 (9), August, pp. 2423–2436
Available at: http://www.tandfonline.com/doi/abs/10.1080/19443994.2014.957982?journalCode=tdwt20
[Accessed 24th July 2016]

Abdulsalam. A, Mohamed. T and Ahsan. A. (2016) An integrated technique using solar and evaporation ponds for effective brine disposal management, *Sustainable Energy*, [online], v.1 (1), January.pp.1-12
Available at: http://www.tandfonline.com/doi/abs/10.1080/14786451.2015.1135923
[Accessed 24th July 2015]

Arafat. H. (2017) *Desalination Sustainability: A Technical, Socioeconomic, and Environmental Approach*. Elsevier. India.

Ahmad. N and Baddour. R. (2014) A review of sources, effects, disposal methods, and regulations of brine into marine environments, *Ocean and Coastal Management*, [online], v.87 (1), January. pp. 1-7
Available at: http://www.sciencedirect.com/science/article/pii/S0964569113002561
[Accessed 24th July 2014]

Arnal. J, Sancho. M, Iborra. I, Goza´ lvez. J, Santafe´. A and Lora. J. (2005) Concentration of brines from RO desalination plants by natural evaporation, *Desalination*, [online], v.182 (3), November, pp.435-439
Available at: http://www.sciencedirect.com/science/article/pii/S0011916405004571
[Accessed 24th July 2014]

Ahmed. M, Shayya. W, Hoey. D, Mahendran. A, Morris. R and Al-Handaly. J. (2000) Use of evaporation ponds for brine disposal in desalination plants, *Desalination*, [online], v.130 (2), November, pp 155-168.
Available at: http://www.sciencedirect.com/science/article/pii/S0011916400000837
[Accessed 24th July 2015]

Ameglio. A, Brioschi. M and Garzoglio. M. (2011) offshore seawater intakes for desalination plants: an operating experience minimizing envirmental impacts, *Proceedings* of the *International Desalination Association*, [online], Italy, 6th June, pp.1-21
Available at: http://www.fisiait.com/pubblicazioni/34/Garzoglio_01%20RevB.pdf
[Accessed 24th July 2014]

Al-Karaghouli. A and Kazmerski. L. (2013) Energy consumption and water production cost of conventional and renewable –powered desalination processes, *Renewable and Sustainable Energy Reviews*, [online], v.24 (1), August, pp.343-356
Available at: http://www.sciencedirect.com/science/article/pii/S1364032113000208
[Accessed 24th July 2015]

Aly. N and El-Fiqi. A. (2003) Mechanical vapor compression desalination systems — A case study, *Desalination*, [online], v.158 (3), August, pp 143-150
Available at: http://www.sciencedirect.com/science/article/pii/S0011916403004442
[Accessed 24th July 2014]

Al-Dousari. A, Al-Ghadban. A and Sturchio. N. (2012) Marine environmental impacts of power desalination plants in Kuwait, *Aquatic Ecosystem Health & Management*, [online], v.15 (10, June, pp.50-55
Available at: http://www.tandfonline.com/doi/full/10.1080/14634988.2012.667336
[Accessed 24th July 2015]

Albatross Fine Chem Ltd. (2004) *Boiler water treatment-frequently Asked questions.* India: Praveen Verma, [online]
Available at: https://books.google.co.uk/books
[Accessed 24th July 2015]

Abuzinada. A, Barth. H, Krupp. F, Böer. B and Al Abdessalaam. T. (2008) *Protecting the Gulf's Marine Ecosystems from Pollution*. Switzerland: Springer Science, [online]
Available at: https://books.google.co.uk/books?
[Accessed 24th July 2015]

A1-Sahlawi. M. (1999) Seawater desalination in Saudi Arabia: economic review and demand projections, *Desalination*, [online], v.123 (3), October, pp.143-147
Available at: http://www.sciencedirect.com/science/article/pii/S0011916499000673
[Accessed 24th July 2014]

Ahmed. M, Shayya. W, Hoey. D and Al-Handaly. J. (2009) Brine disposal from Inland Desalination Plants Research Needs Assessment, *International Water Resources Association*, [online], v.27 (2), Jun, pp.194-201
Available at: http://www.tandfonline.com/doi/pdf/10.1080/02508060208686992
[Accessed 24th July 2014]

Ahmed. M, Shayya. W, Hoey. D and Al-Handaly. J. (2001) Brine disposal from reverse osmosis desalination plants in Oman and the United Arab Emirates, *Desalination*, [online], v.133 (2), March, pp.135-147
Available at: http://www.sciencedirect.com/science/article/pii/S0011916401800047
[Accessed 24th July 2014]

Wahab. S and Al-Weshahi. M. (2009) Brine Management: Substituting Chlorine with On-Site Produced Sodium Hypochlorite for Environmentally Improved Desalination Processes, *Water Resources Management*, [online], v.23 (12), January, pp.2437-2454
Available at: http://link.springer.com/article/10.1007%2Fs11269-008-9389-7
[Accessed 24th July 2014]

Alghariani. S, (2007) Reducing agricultural water demand in Libya through the improvement of water use efficiency and crop water productivity. *Proceedings of the International Conference WASAMED Project*, [online], Valenzano. Italy, 14 January, v.1 (56), pp.99-107.
Available at: http://om.ciheam.org/article.php?IDPDF=800105
[Accessed 24th July 2015]

Abughlelesha. M and Lateh. H. (2013) A Review and Analysis of the Impact of Population Growth on Water Resources in Libya, World Applied Sciences, [online], v.23 (7), July, pp. 965-971
Available at: https://pdfs.semanticscholar.org/bd36/43cfe0037d52bd0a8a4398af531049ef998d.pdf
[Accessed 24th July 2014]

Alhabishe. A. (2012) Interview by Ali Elhajaji. Gharyan. Libya. 12 May 2012.

Abulqasem. A. (2012) Interview by Ali Elhajaji. Tripoli. Libya. 10 May 2012.

Abdudayem. A and Scott. A. (2014) Water infrastructure in Libya and the water situation in agriculture in the Jefara region of Libya, *African Journal of Economic and Sustainable Development (AJESD)*, [online], v.3 (1), May, pp.33-64
Available at: http://econpapers.repec.org/article/idsajesde/v_3a3_3ay_3a2014_3ai_3a1_3ap_3a33-64.htm
[Accessed 24th July 2015]

Al habashi. A. (2012) Interview by Ali Elhajaji. Gharyan. Libya. 14 May 2012

Abdelrhem. I, Rashid. K and Ismail. A. (2008) Integrated Groundwater Management for Great Man-Made River Project in Libya, *Scientific Research*, [online], v.22 (4), January, pp.562-569
Available at: http://www.yemenwater.org/wp-content/uploads/2013/03/Abdelrhem-Isam-Mohamed-Rashid-Kahlim-and-Ismail-Amiruddin-2008.pdf

[Accessed 24th July 2015]

Al Farrah. N, Martens. K and Walraevens. K. (2011) hydrochemistry of the upper Miocene-Pliocene-quaternary aquifer complex of Jifarah plain, NW- Libya, *Geologica Belgica*,[online], v.14 (4), October, pp.159-174.
Available at: https://biblio.ugent.be/publication/1204647
[Accessed 24th July 2014]

Andrianne. J and Alardin. F. (2002) Thermal and membrane processes economics: selection for seawater desalination optimized, *Journal of Desalination*, [online], v.153 (3), February, pp.305-311,
Available at: http://www.sciencedirect.com/science/article/pii/S0011916402011281
[Accessed 24th July 2014]

Al-Shayji. K. (1998) *Modelling, simulation and optimization of large-scale commercial desalination plants, PhD Thesis*: *Chemical Engineering, Virginia Polytechnic Institute and State University*, April, pp.1-453
Available at: http://scholar.lib.vt.edu/theses/available/etd-32898-13261/unrestricted/ETD.PDF
[Accessed 24th July 2014]

Anthoni. J. (2006) *The chemical composition of seawater*, [online],
Available at: http://www.seafriends.org.nz/oceano/seawater.htm
[Accessed 24th July 2014]

Ahwide. F and Aldali. Y. (2013) The Current Situation and Perspectives of Electricity Demand and Estimation of Carbon Dioxide Emissions and Efficiency, Environmental, Ecological, *Geological and Geophysical Engineering*, [online], , v.7 (12), January, pp. 698-703
Available at: http://waset.org/publications/9997922/the-current-situation-and-perspectives-of-electricity-demand-and-estimation-of-carbon-dioxide-emissions-and-efficiency
[Accessed 24th July 2014]

Anezi. K and Hilal. N. (2007) Scale formation in desalination plants: effect of carbon dioxide solubility, *Journal of Desalination*, [online], v. 204 (3), February, pp.385-402
Available at: http://www.sciencedirect.com/science/article/pii/S0011916406013440
[Accessed 24th July 2014]

Abdelwahab. M and Hamoda. A. (2012) Effect of desalination plants on the marine environment along the red sea, Egypt. (Case study), *Journal of Marine Sciences*, [online], v.28 (2), July, pp.27-36
Available at: http://webs.uvigo.es/thalassas/Thalassas%2028(2)/Art.%203%20Thalassas%2028(2).pdf
[Accessed 24th July 2014]

Al-Mutaz. I. (2013) *Environmental impact of seawater desalination plants: Common fundamentals and unit operations in thermal desalination systems* [online]
Available at: - http://www.desware.net/sample-chapters/d02/d00-010.pdf
[Accessed 24th July 2014]

Afgan. N, Darwish. M and Garvalho. M. (1999) Sustainability assessment of desalination plants for water production. *Desalination*, [online], v.124 (3), November, pp. 19-31.
Available at: http://www.sciencedirect.com/science/article/pii/S0011916499000855
[Accessed 24th July 2014]

Ahmed. M and Anwar. R. (2012) An Assessment of the Environmental Impact of Brine Disposal in Marine Environment, *Modern Engineering Research*, [online], v.2 (4), July, pp-2756-2761
Available at:- http://www.ijmer.com/papers/Vol2_Issue4/EX2427562761.pdf
[Accessed 24th July 2014]

Al-Barwani. H and Purnama. A, (2007) Re-assessing the impact of desalination plants brine discharges on eroding beaches, *Desalination.* [online], v. 204 (3), February, pp.94-101
Available at: http://www.sciencedirect.com/science/article/pii/S0011916406013105
[Accessed 24th July 2014]

Asokan. K and Subramanian. K (2009) Design of a Tank Electrolyser for In-situ Generation of NaClO, *Proceedings of the World Congress on Engineering and Computer Science.* [online], San Francisco, v. I (1), October, pp.1-4,
Available at: http://www.iaeng.org/publication/WCECS2009/WCECS2009_pp139-142.pdf
[Accessed 24th July 2014]

Alagha. A. (2010) *Hypochlorite Generation On Some Modified Electrodes For Treatment Of Wastewater Pollutants*. [online], MSc. Thesis, Al-Azhar University of Gaza. pp.1-90,
Available at: http://webcache.googleusercontent.com/search?q=cache:7JfaMXMJbCEJ:www.alazhar.edu.ps/Library/aattachedFile.asp%3Fid_no%3D0043708+&cd=18&hl=en&ct=clnk&gl=uk
[Accessed 24th July 2014]

Andrews. A. (1983) *Maya Salt production and Trade*. University of Arizona press, Tucson.

Akridge. D. (2008) Methods for calculating brine evaporation rates during salt production, *Archaeological Science*, [online], v.35 (6), June,pp.1453-1462
Available at: http://www.sciencedirect.com/science/article/pii/S0305440307001987
[Accessed 24th July 2015]

Abdulgader. A and Mustafe. G. (1998) *Performance evaluation of Belgard EV2050 at al-Aziza reheat plant, Research and Development Centre, Saline Water Conversation Corporation*; *Technical Report No. TR-3808/EVP96004,* [online], October. pp. 1786- 1804
Available at: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.540.3510&rep=rep1&type=pdf
[Accessed 24th July 2015]

Allen. R, Pereira. L, Raes. D and Smith. M. (2008), Crop evapotranspiration-Guidelines for computing crop water requirements- FAO Irrigation and Drainage Paper 56, Food and Agriculture Organization, Rome. [online], pp.1-15
Available at: http://s3.amazonaws.com/academia.edu.documents/40878584/Allen_FAO1998.pdf?AWSAccessKeyId=AKIAJ56TQJRTWSMTNPEA&Expires=1474558936&Signature=g40D%2BtjZrK5HVqeSBHSKONCDaLE%3D&response-content-disposition=inline%3B%20filename%3DAllen_FAO1998.pdf
[Accessed 24th July 2015]

Addala. S, Bouhdjer. L, Chala. A, Bouhdjar. A,Halimi.O, Boudine. B, Sebais. M. (2013) Structural and optical properties of a NaCl single crystal doped with CuO nanocrystals. *Science and Technology*. [online], March, v.22 (9), pp.1-5.
Available at: http://cpb.iphy.ac.cn/EN/abstract/abstract55314.shtml
[Accessed 24th July 2015]

Barnett. T, Pierce. D and Schnur. R. (2001) Detection of Anthropogenic Climate Change in the World's Oceans, Science, [online], v.292 (5515), pp. 270-274
Available at: http://science.sciencemag.org/content/292/5515/270
[Accessed 24th July 2017]

Barron. O, Ali. R, Hodgeson. G, Smith. D, Qureshi. E, Mcfarlan. D, Campos. E, Zarzo. D. (2015) Feasibility assessment of desalination application in Australian traditional agriculture, *Desalination*, [online], v.364 (1), May. Pp.33-45
Available at: http://www.sciencedirect.com/science/article/pii/S0011916414004056
[Accessed 24th July 2017]

Bargues. J. (2014) Analysis of the process of environmental impact assessment for seawater desalination plants in Spain, *Desalination*, [online], v.347 (1), August, pp.166-174
Available at: http://www.sciencedirect.com/science/article/pii/S0011916414002999
[Accessed 24th July 2014]

Belessiotis.V, Kalogirou. S and Delyannis. E (2016) *Thermal Solar Desalination Methods and Systems*. USA. Academic Press Elsevier Ltd

Bleninger. T and Jirka. G (2008) Modelling and environmentally sound management of brine discharges from desalination plants, *Desalination*, [online], v.221 (3), pp.585-597
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407007448
[Accessed 24th July 2015]

Bleninger. T, Niepelt. A and Jirka. G (2010) Desalination plant discharge calculator, *Desalination and Water Treatment*, [online], v.13 (3), August, pp.156-173
Available at: http://www.tandfonline.com/doi/abs/10.5004/dwt.2010.1055
[Accessed 24th July 2015]

Brika. B, Omran. A and Addien. O. (2016) Chemical elements of brine discharge from operational Tajoura reverse osmosis desalination plant, *Desalination and Water Treatment*, [online], v.57 (12)
Available at :
http://www.tandfonline.com/doi/abs/10.1080/19443994.2014.1003330
[Accessed 24th July 2014]

Buros. O. (1990) *The Desalting ABC, International Desalination Association*, Topsfield, MA, USA
Available at: http://www.water.ca.gov/pubs/surfacewater/abcs_of_desalting/abcs_of_desalting.pdf
[Accessed 24th July 2014]

Balasubramanian. P. (2013) A brief review on best available technologies for reject water (brine) management in industries, Environmental Science, [online], v.3 (6), June.pp.2010-2013.
Available at: http://connection.ebscohost.com/c/articles/90566538/brief-review-best-available-technologies-reject-water-brine-management-industries
[Accessed 24th July 2014]

Bindra. S, Hamid. A, Salem. H, Hamuda. K, Abulifa. S. (2014) Sustainable Integrated Water Resources Management for Energy Production and Food Security in Libya, *Procedia Technology: The 7th International Conference Interdisciplinary in Engineering*, [online], v.12 (1), January, pp.747-752
Available at: http://www.sciencedirect.com/science/article/pii/S2212017313007433
[Accessed 24th July 2014]

Bindra. S, Abulifa. S, Hamid. A, Al-Reiani. H and Abdalla. H. (2013) Assessment of impacts on ground water resources in Libya and vulnerability to climate change, *Water supply and irrigation systems*, [online], v.10 (2), January, pp.63-69
Available at: http://eds.a.ebscohost.com/eds/pdfviewer/pdfviewer?sid=d82bb493-8e56-47b1-a86b-f442f848d8a0%40sessionmgr4006&vid=1&hid=4105
[Accessed 24th July 2015]

Bureau of Statistics and Census Libya. (2013) *State of Libya: Statistical Report: Population Growth. Tripoli. Libya. In Arabic version*

Bureau of Statistics and Census Libya. (2012) *State of Libya: Statistical Report: Quantity of Drinking Water. Tripoli. Libya,* [online].
Available at: http://bsc.ly/?P=5&sec_Id=15&dep_Id=4#74
[Accessed 24th July 2015]

Bunta. J. (2010) *Libya's Great Man-Made River*, [online]
Available at: http://www.boinc.sk/clanky/libyas-great-man-made-river
[Accessed 24th July 2015]

Beer. S and Waisel. Y. (1979) Some photosynthetic carbon fixation properties of seagrasses, *Aquatic Botany*, [online], v.7 (1), March, pp.129–138
Available at: http://www.sciencedirect.com/science/article/pii/0304377079900172

Boyed. C and Tucker. C. (1998) Pond Aquaculture Water Quality Management. USA. Kluwer Academic

Borum. J, Duarte. C, Jensen. D and Greve. T. (2004) *European seagrasses: an introduction to monitoring and management: Report, EU project Monitoring and Managing of European Seagrasses (M&MS) EVK3-CT-2000-00044*, [online], September, pp.1-98
Available at: http://www.seagrasses.org/
[Accessed 24th July 2014]

Bonanno. A, Zgozi. S and Bahri. T. (2006) *Report of the MedSudMed-06 Oceanographic Survey, Strait of Sicily, Libyan continental shelf, MedSudMed Component on "Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their abundance and distribution", MedSudMed Technical Document*s, [online], August, pp.1-67.
Available at:- http://www.faomedsudmed.org/pdf/publications/TD27.pdf
[Accessed 24th July 2014]

Benkhayal. A, Elshrrif. K and El-turki. K. (2013) Determination of some heavy metals in seagrass "Posidonia oceanica"(L.) Delile of Benghazi Coast in Libya "Mediterranean", *Journal of Marine Sciences*, [online], v. 4 (5), January ,pp.1-6, Available at: http://pelagiaresearchlibrary.com/der-chemica-sinica/vol4-iss5/DCS-2013-4-5-1-6.pdf,
[Accessed 24th July 2014]

Bashtan. S, Goncharuk. V, Chebotareva. R, Belyakov. V and Linkov. V. (1999) Production of sodium hypochlorite in an electrolyser equipped with a ceramic membrane, *Desalination*. [online], v.126 (3), November. pp. 77-82
Available at: http://www.sciencedirect.com/science/article/pii/S0011916499001563
[Accessed 24th July 2014]

Burney. H, Furuya. N, Hine. F and Ota. K (1999) *Electrolytic Sodium Chlorate Technology: Current Status;* Electrochemical Society, United States of America

Batterson. M. and Boddie. W. (1972) *Salt, the Mysterious Necessity*, United States of America. Dow Chemical Co.

Boxwell. M. (2016) *Solar Electricity Handbook: A simple, practical guide to solar energy design and installing solar PV system*, Greenstream Publishing Limited, United Kingdom.
http://www.solarelectricityhandbook.com/solar-irradiance.html

Benzaghat. M, Mohammed. T, Ghazali. Abdul and Soom. M. (2011) Comparison of evaporation estimate models for surface evaporation in semi-arid region of Libya: A case study. *Canadian Journal of Civil Engineering.* [online], November, v.38 (12), pp. 1373-1380. Available at:
http://www.nrcresearchpress.com/doi/abs/10.1139/l11-098#.WJP1BvmLTct
[Accessed 24th July 2015]

Butts. D. (2011) *Elements of mineral production from brine in solar ponds, DSB International Inc*, [online], pp. 1-11,
Available at: www.dsbinternational.com
[Accessed 24th July 2015]

Council of Europe. (2012) *Biodiversity and Climate Change: Reports and Guidance Developed Under the Bern Convention: Nature and Environment No.160: volume 2,* [online]. Strasbourg. Council of Europe
Available at:
https://books.google.co.uk/books?id=EsWT8Ukcq48C&printsec=frontcover&source=gbs_ge_summary_r&cad=0#v=onepage&q&f=false
[Accessed 24th July 2017]

Cipollina. A, Micale. G and Rizzuti. L. (2009) *Seawater Desalination: Conventional and Renewable Energy Processes: Green Energy and Technology.* Springer: Berlin

Castriota. L, Beltrano. M, Giambalvo. O and Sunseri. G. (2001) A one-year study of the effects of a hyperhaline discharge from a desalination plant on the zoobenthic communities in the Ustica Island Marine Reserve (Southern Tyrrhenian Sea), [online], CIESM Congress, Monte Carlo, Monaco, 4. Italy
Available at:
https://www.researchgate.net/profile/Luca_Castriota/publication/260037530_Effects_of_a_hyperhaline_discharge_from_a_desalination_plant_on_the_zoobenthic_communities_over_one_year_in_the_Ustica_Marine_Reserve_Southern_Tyrrhenian_Sea/links/558aa8f908ae31beb0ffeb01/Effects-of-a-hyperhaline-discharge-from-a-desalination-plant-on-the-zoobenthic-communities-over-one-year-in-the-Ustica-Marine-Reserve-Southern-Tyrrhenian-Sea.pdf
[Accessed 24th July 2014]

Cipollina. A, Misseri. A, Staiti. G, Galia. A. Micale. G and Scialdone. O. (2012) Integrated production of fresh water, sea salt and magnesium from sea water, *Desalination and Water Treatment*, [online], v.49 (3), May. pp. 390–403
Available at: http://www.tandfonline.com/doi/abs/10.1080/19443994.2012.699340
[Accessed 24th July 2015]

Cipollina. A, Misseri. A, Staiti .A, Galia. A, Micale. G and Scialdone. O. (2012). Integrated production of fresh water, sea salt and magnesium from sea water. *Desalination and Water Treatment*,[online], v. 49 (3),Jun, pp.390-403.
Available at : http://www.tandfonline.com/doi/abs/10.1080/19443994.2012.699340?journalCode=tdwt20
[Accessed 24th July 2014]

Cooley. H, Gleick. P and Wolff. G. (2006) *Desalination, with a grain of salt a California perspective: Pacific institute*, [online], June, pp. 1-87.
Available at: http://pacinst.org/app/uploads/2015/01/desalination-grain-of-salt.pdf
[Accessed 24th July 2014]

Cipollina. A, Micale. G and Rizzuti. L. (2009) *Seawater Desalination: Conventional and Renewable Energy Processes: Green Energy and Technology*. Springer: Berlin

Cotruvo. J, Fawell. J, Cunliffe. D, Voutchkov. N, Payment. P and Lattemann. S. (2010) *Desalination technology: Health and Environmental Impacts*. United States of America: Taylor and Francis Group

Compain. P. (2012) Solar Energy for Water desalination, *Procedia Engineering*, [online], France, v.46 (1), January, pp. 220-227
Available at: http://www.sciencedirect.com/science/article/pii/S1877705812045316
[Accessed 24th July 2014]

Colley. H and Ajami. N. (2012) *Key issues for desalination in California: cost and financing. Pacific Institute: Oakland. California*, [online], November, pp.4-46
Available at: http://pacinst.org/app/uploads/2013/02/financing_final_report3.pdf
[Accessed 24th July 2014]

Carollo. (2009) *Water desalination concentrate management and piloting; South Florida Water Management District*, [online], December, pp.1-125Available at: http://www.sfwmd.gov/portal/page/portal/xrepository/sfwmd_repository_pdf/waterdesalinationconcentratemgmtpiloting-dec09-carollo.pdf
[Accessed 24th July 2014]

Cuence. C. (2012) Report on Water Desalination Status in the Mediterranean Countries, [online], September.

Available at: http://www.imida.es/documents/13436/877249/06_REPORT_ON_WATER+DESALINATION.pdf/ae6203f4-68f9-4a37-b728-22b5d247909e
[Accessed 24th July 2014]

Cedare. (2014) "*Libya Water Sector M&E Rapid Assessment Report", Monitoring and Evaluation for Water In North Africa (MEWINA) Project, Water Resources Management Program, CEDARE*.
Available at: http://web.cedare.org/wp-content/uploads/2005/05/Libya-Water-Sector-Monitoring-and-Evaluation-Rapid-Assessment-Report.pdf
[Accessed 24th July 2015]

Clarke K.R. and Gorley R.N. (2006) *PRIMER v6: User manual/Tutorial*. PRIMER-E Ltd., Plymouth.

Clarke K.R. (1993) Non-parametric multivariate analyses of changes in community structure. *Australian Journal of Ecology*, [online], v 18 (1), March 117-143
Available at: http://onlinelibrary.wiley.com/doi/10.1111/aec.1993.18.issue-1/issuetoc
[Accessed 24th July 2014]

Chapman. M and Underwood. A. (1999) Ecological patterns in multivariate assemblages: information and interpretation of negative values in ANOSIM tests, *Journal of Marine Ecology*, [online], v.180 (1), March, pp.257-265,
Available at: http://www.int-res.com/articles/meps/180/m180p257.pdf
[Accessed 24th July 2014]

Caldira. K and Wickett. M. (2003) Oceanography: Anthropogenic carbon and ocean pH, *Journal of Science*, [online], v.425, September, pp.365
Available at: http://www.nature.com/nature/journal/v425/n6956/full/425365a.html
[Accessed 24th July 2014]

Connor. M, Bruno. J, Gaines. S, Halpern. B, Lester. S, Kinlan. B and Weiss. J. (2007) Temperature control of larval dispersal and the implications for marine ecology, evolution, and conservation**,** *National Academy of Sciences*, [online], v. 104 (4), January, pp.1266-1271
Available at: - http://www.pnas.org/content/104/4/1266.full.pdf
[Accessed 24th July 2014]

Canadian Council of Ministers of the Environment (1999) *Canadian Water Quality Guidelines for the Protection of Aquatic Life: Dissolved oxygen (Marine)* [online], pp.1-5,
Available at: file:///C:/Users/user/Downloads/Dissolved%20Oxygen%20(Marine)%20(en).pdf
[Accessed 24th July 2014]

Calleja. M, Barron. C, Hale. J, Frazer. T and Duarte. C. (2006) Light Regulation of Benthic Sulphate Reduction Rates Mediated by Seagrass (Thalassia testudinum)

Metabolism, *Journal of Estuaries and Coasts*, [online], v.29 (6), December, pp.1255-1264.
Available at: http://link.springer.com/article/10.1007/BF02781825
[Accessed 24th July 2015]

Choi. J, Shim. S and Yoon. J. (2013) Design and operating parameters affecting an electrochlorination system, *Journal of Industrial and Engineering Chemistry*, [online], v.19 (1), January, pp 215-219.
Available at: http://www.sciencedirect.com/science/article/pii/S1226086X12002638
[Accessed 24th July 2014]

Cyprtaa. S, Benwd. A and Allenbgle. N. (2013) The use of electro-coagulation in seawater desalination system, *Engineering Sciences*, in Arabic Version, [online], v.29 (1), pp.393-403
Available at: http://www.damascusuniversity.edu.sy/mag/eng/images/stories/1-2013a/wew/393-403.pdf,

Cipollina. A, Misseri. A, Staiti. G, Galia. A. Micale. G and Scialdone. O. (2012) Integrated production of fresh water, sea salt and magnesium from sea water, *Desalination and Water Treatment*, [online], v.49 (3), May. pp. 390–403
Available at: http://www.tandfonline.com/doi/abs/10.1080/19443994.2012.699340
[Accessed 24th July 2015]

Dupavillon. J and Gillanders. B. (2009) Impacts of seawater desalination on the giant Australian cuttlefish Sepia apama in the upper Spencer Gulf, South Australia, *Marine Environmental Research*, [online], v.67 (5), May, pp.207-218
Available at: http://www.sciencedirect.com/science/article/pii/S0141113609000257?via%3Dihub
[Accessed 24th July 2015]

Darwish. M, Hassabou. A, Shomar. B. (2013) Using Seawater Reverse Osmosis (SWRO) desalting system for less environmental impacts in Qatar, *Desalination*, [online], v.309 (1), January,pp.113-124
Available at: http://www.sciencedirect.com/science/article/pii/S0011916412005413
[Accessed 24th July 2015]

Dweiri. S and Badran. M. (2002) Desalination: an imminent solution for the future water needs in the Aqaba Special Economic Zone (ASEZ), *Desalination*, [online], v.152 (3), pp.27-39
Available at: http://www.sciencedirect.com/science/article/pii/S0011916402010457
[Accessed 24th July 2015]

Darwish. M, Jawad. M and Aly. G. (1989) Technical and economic comparison between large capacity MSF and RO desalting plants, *Desalination*, [online], v.76 (1), January, pp. 281-304
Available at: http://www.sciencedirect.com/science?
[Accessed 24th July 2014]

Davis. T. (2006) *Zero Discharge Seawater Desalination: Integrating the Production of Freshwater, Salt, Magnesium, and Bromine. Desalination and Water Purification Research Development Program Report No. 111,* [online], May, pp.1-32
Available at: http://www.cacoastkeeper.org/document/zero-discharge-seawater-desalination.pdf
[Accessed 24th July 2014]

Dimkic. M, Brauch. H and Kavanaugh. M. (2008) G*roundwater Management in Large River Basins*, [online]. London. UK: The International Water Association
Available at: https://books.google.co.uk/books?id
[Accessed 24th July 2015]

Davis. D. (2015) *Water quality: What is the water quality, Kent State University, Lake Scientist*, [online],
Available at: http://www.lakescientist.com/lake-facts/water-quality/
[Accessed 24th July 2015]

Dean. C. (2009) *Rising acidity is threatening food web of oceans, science panel says*, [online],
Available at: http://www.nytimes.com/2009/01/31/science/earth/31ocean.html?_r=0
[Accessed 24th July 2015]

Davis. J. (2000) Structure, function, and management of the biological system for seasonal solar saltworks, *Global Nest*, [online], v.2 (3), January. pp. 217-226
Available at: http://journal.gnest.org/sites/default/files/Journal%20Papers/davis.pdf
[Accessed 24th July 2015]

Deegan. L, Johnson. D, Warren. R, Peterson. B, Fleeger. J, Fagherazzi. S and Wollheim. W, (2012) Coastal eutrophication as a driver of salt marsh loss, *Science*, [online], v. 490 (1), October, pp.388-392.
Available at: http://www.nature.com/nature/journal/v490/n7420/pdf/nature11533.pdf
[Accessed 24th July 2015]

Dardir. A and Wali. A. (2006) Extraction of salts from lake Quaroun, Egypt: Environmental and economic impacts. *Proceedings of the 1st International Conference on the Ecological Importance of Solar Saltworks,* [online], Santorini Island, Greece,20-22, October, pp. 44-51.
Available at: http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=7852
[Accessed 24th July 2015]

Delanuez. F, Suárez. N, Santiago. D, Veza. J and Sadhwani. J. (2012) Reuse and minimization of desalination brines: a review of alternatives, *Desalination and Water Treatment*, [online], v.39 (3), February, pp.137-148
Available at: http://www.tandfonline.com/doi/abs/10.1080/19443994.2012.669168
[Accessed 24th July 2015]

Elabbarb. M and Elmabrouka. F. (2005) Environmental impact assessment for desalination plants in Libya. Case study: Benghazi North and Tobrouk desalination plants, *Desalination*, [online], v.185 (3), November, pp.31-44
Available at: http://www.sciencedirect.com/science/article/pii/S0011916405006065
[Accessed 24th July 2014]

Eslamian. S. (2016) *Urban Water Reuse Handbook*, CRC Press. USA

Elabbar. M. (2008) The Libyan experimental on the environmental impact assessment for desalination plants, Desalination, [online], v.220 (3), March, pp.24-36
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407006029
[Accessed 24th July 2015]

Elhassadi. A. (2013) General Desalination Company of Libya (GDCOL), Libya Report, [online], 8.8.2013.
Available at: http://www.marcopolis.net/gdcol-plans-to-increase-libyas-desalination-capacity-by-building-more-desalination-plants.htm
[Accessed 24th July 2015]

Einav. R, Harussi. K and Periy. D. (2003) The footprint of the desalination processes on the environment, *Desalination*, [online], v.152 (3), February, pp.141-154
Available at: http://www.sciencedirect.com/science/article/pii/S0011916402010573
[Accessed 24th July 2014]

Eltawil. M, Zhengming. Z and Yuan. L. (2009) A review of renewable energy technologies integrated with desalination systems, *Renewable and Sustainable Energy Reviews*, [online], v.13 (9), December, pp.2245-2262
Available at: http://www.sciencedirect.com/science/article/pii/S1364032109000987
[Accessed 24th July 2014]

Einav. R, Harussi. K and Perry. D. (2002) The foot prints of the desalination processes on the environment. *Desalination*, [online], v.152 (1), April, pp.141-154.

Available at: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.558.7619&rep=rep1&type=pdf
[Accessed 24th July 2014]

El-Naas. M. (2011) *Reject Brine Management, Desalination, Trends and Technologies, in Schorr. M, Chemical Engineering*, DOI: 10.5772/13706, InTech, [online], February, pp.238-243
Available at: http://www.intechopen.com/books/desalination-trends-and-technologies/reject-brine-management
[Accessed 24th July 2014]

Elabbar. M and Elmabrouk. F. (2005) Environmental impact assessment for desalination plants in Libya. Case study: Benghazi North and Tobrouk desalination plants, *Desalination*, [online], v.185 (3), November, pp.31-44
Available at: http://www.sciencedirect.com/science/article/pii/S0011916405006065
[Accessed 24th July 2015]

El Asswad. R. (1995) Agricultural Prospects and Water Resources in Libya, *Journal of agricultural*, [online], v. 24 (6), September, pp. 324-327
Available at: http://www.jstor.org/stable/4314361?seq=2 [Oct.25, 2012].
[Accessed 24th July 2015]

Einav. R and Lokiec. F. (2003) Environmental aspects of desalination plant in Ashkelon, *Journal of Desalination*, [online], v.156 (3), August, pp.79-85
Available at: http://www.sciencedirect.com/science/article/pii/S001191640300328X
[Accessed 24th July 2014]

Elfallah. M and Bosrgob. A. (2005) *United Nation Environment Program: The National Action PLAN For the Libyan Coastal Area*, [online], pp.1-55
Available at: http://www.themedpartnership.org/med/documents/library/background-documents/naps/en/attachments%7Cattachments%3A011%7Cfile
[Accessed 24th July 2015]

Enka. (2013) *Enka in Libya: Libya projects*, [online]
Available at: http://www.enka.com/en/wp-content/uploads/2017/01/ENKA_IN_LIBYA.pdf
[Accessed 24th July 2015]

European Union. (2012) *Assessment of potential cumulative environmental impacts of mega desalination plants conglomerating around the Mediterranean under the pillar non- conventional water resources, Sustainable Water Integrated Management (SWIM) - Support Mechanism*, [online], October, pp.1-7
Available at: file:///C:/Users/bueaelha/Downloads/concept%20note%20desalination.pdf
Exadactylos. A. (2015) *Molecular Approach of Seagrasses Response Related to Tolerance Acquisition to Abiotic Stress: Molecular Approaches to Genetic*

Diversity, Agricultural and Biological Sciences, Prof. Mahmut Caliskan (Ed.), InTech, DOI: 10.5772/59425,[online], April, pp.76-91
Available at: http://www.intechopen.com/books/references/molecular-approaches-to-genetic-diversity/molecular-approach-of-seagrasses-response-related-to-tolerance-acquisition-to-abiotic-stress
[Accessed 24th July 2015]

Elsaid. K, Bensalah. N and Wahab. A. (2012) Inland Desalination: Potentials and Challenges, Advances in Chemical Engineering, Dr Zeeshan Nawaz (Ed.), InTech, DOI: 10.5772/33134, [online], March, pp.450-480,
Available at: http://www.intechopen.com/books/advances-in-chemical-engineering/inland-desalination-potentials-and-challenges
[Accessed 24th July 2015]

Environmental International Consultants (2009) *Environmental Impact Assessment for Jebel Ali Power and Desalination Station M*, [online], April, pp.1-140,
Available at: http://www.agaportal.de/pdf/nachhaltigkeit/eia/eia_dubai_kraftwerk.pdf
[Accessed 24th July 2015]

El-Magsodi. M and Haddoud. D. (2010) *The Salt Marsh (Sabka) in the Western part of Libya*, in Öztürk. M, Böer. B, Barth. H, Breckle. S. Godt. M and Khan, M. *Sabkha Ecosystems: Volume III: Africa and Southern Europe: 3 (Tasks for Vegetation Science)*, Springer, London. pp. 79-84

Foster. S. (2001) The interdependence of groundwater and urbanisation in rapidly developing cities, *Urban Water*, [online], v.3 (3), September, pp.185-192
Available at: http://www.sciencedirect.com/science/article/pii/S1462075801000437
[Accessed 24th July 2017]

Frich. P, alexander. L, Marta. P, Gleason. B, Haylock. M, Tank. A and Peterson. T. (2002) Observed coherent changes in climatic extremes during the second half of the twentieth century, *Climate Research*, [online], v.19 (3), January, pp. 193–212
Available at: http://www.int-res.com/abstracts/cr/v19/n3/p193-212/
[Accessed 24th July 2017]

Frank. H, Rahav. E and Bar-Zeev. E. (2017) Short-term effects of SWRO desalination brine on benthic heterotrophic microbial communities, *Desalination*, [online], v.417 (1), September. Pp.52-59
Available at: http://www.sciencedirect.com/science/article/pii/S0011916416321749
[Accessed 24th July 2015]

Fritzmann. C, Löwenberg. J, Wintgens. T, Melin. T. (2007) State-of-the-art of reverse osmosis desalination, *Desalination*, [online], v.216 (3), October, pp.1-76
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407004250

[Accessed 24th July 2015]

Fath. H, Elsherbiny. S, Hassan. A, Rommel. M, Wieghaus. M, Koschikowski. J and Vatansever.M. (2008) PV and thermally driven small-scale, stand-alone solar desalination systems with very low maintenance needs. *Desalination,* [online], v.225 (3), May, pp.58-69
Available at: http://www.sciencedirect.com/science/article/pii/S0011916408000908
[Accessed 24th July 2014]

Fellows. C and Al-Hamzah. A. (2015) Thermal Desalination: Current Challenges. In Amjad. Z and Demadis. Konstantinos, *Mineral Scales and Deposits: Scientific and Technological Approaches*. Oxford. UK. Elsevier, pp. 583-599

Fath. H and Ghazy. A. (2002) Solar desalination using humidification—dehumidification technology, Desalination, [online], v.142 (2), February, pp.119-113
Available at: http://www.sciencedirect.com/science/article/pii/S0011916401004313
[Accessed 24th July 2014]

Fabry. V., Seibel. B, Feely. R, and Orr. J (2008) Impacts of ocean acidification on marine fauna and ecosystem processes, *Journal of Marine Science*, [online], v. 65 (1), April, pp. 414–432.
Available at: https://academic.oup.com/icesjms/article/65/3/414/789605/Impacts-of-ocean-acidification-on-marine-fauna-and?searchresult=1
[Accessed 24th July 2015]

Faragallah. H, Askar. A, Okbah. M and Moustafa. H. (2009) Physico-chemical characteristics of the open Mediterranean Sea water for about 60 km from Damietta harbor, Egypt**,** *Journal of Ecology and The Natural Environment*,[online],v.1(5), August,pp.106-119
Available at: http://www.academicjournals.org/JENE,
[Accessed 24th July 2014]

Field. A. (2013) *Discovering Statistics Using IBM SPSS Statistics*. 4th ed. London SAGE publication Ltd.

Folk. R. (1974) *Petrology of Sedimentary Rocks. Austin, Texas*: Hemphill Publishing Company

Flad. R, Zhu. J, Wang. C, Chen. P, Falkenhausen. L, Sun. Z and Li. S. (2005) Archaeological and chemical evidence for early salt production in China, *The National Academy of Sciences of the United States of America,* [online], v.102 (35), July, pp.12618-12622.
Available at: http://www.pnas.org/content/102/35/12618.full.pdf
[Accessed 24th July 2015]
Google earth, (2016) Online image by researcher

General Water Authority (2004) *Water Situation in Libya: Tripoli. Libya. In Arabic version.*

General Desalination Company of Libya. (2013) A brief about the GDCOL. *In Arabic version*
Available at: http://www.gdcol.ly/aboutus.php
[Accessed 24th July 2015]

Giwa. A, Dufour. V, Al Marzooqi. F, Al Kaabi. M and Hasan. S. (2017) Brine management methods: Recent innovations and current status, *Desalination*, [online], v.407 (1), April, pp.1-23
Available at: http://www.sciencedirect.com/science/article/pii/S0011916416305306
[Accessed 24th July 2014]

Gálvez. J, Rodríguez. S, Delyannis. E, Belessiotis. V, Bhattacharya. S and Kumar. S. (2010) *Solar energy conversion and photoenergy systems: thermal systems and desalination plants-volume III*. United Kingdom: EOLSS Publications

Glueckstern. P and Priel. M. (1996) Optimized Brackish Water Desalination Plants with Minimum Impact on the Environment, *Desalination* [online], v. 108 (3), Feburary.pp.19-26
Available at: http://www.sciencedirect.com/science/article/pii/S0011916497000040
[Accessed 24th July 2014]

Glater. J and Cohen. Y. (2003) *Brine disposal from land based membrane desalination plants: A critical Assessment. Draft Prepared for the Metropolitan Water District of Southern California, Polymer and Separations Research Laboratory University of California, Los Angeles*, [online], July, pp. 1-16
Available at: http://www.lesico-cleantech.com/pdf/brine_disposal_article_ucla.pdf
[Accessed 24th July 2014]

Gilron. J, Folkman. Y, Savliev. R, Waisman. M. Kedem. O (2003) WAIV—wind aided intensified evaporation for reduction of desalination brine volume. *Desalination*, [online]. v.158 (3), August. pp. 205-2014
Available at: http://www.sciencedirect.com/science/article/pii/S0011916403004533
[Accessed 24th July 2014]

Gibbons. J Papapetrou. M and Epp. C. (2008) Assessment of EU policy: Implications for the implementation of autonomous desalination units powered by renewable resources in the Mediterranean region, *Desalination*, [online], v.220 (3), March.pp.422-430
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407006418
[Accessed 24th July 2014]

Great Man-Made River Authority (2012) *Report about the GMRP: Implementation and Management of the GMRP: Tripoli. Libya. In Arabic version.*

General Electric Company of Libya. (2015) A brief about the GECOL: Implementation and Management of the GECOL. *Tripoli. Libya. In Arabic version* Available at: https://www.gecol.ly/GECOL_LY/about.aspx
[Accessed 24th July 2015]

General environment Authority. (2011) *A brief report about the General environment Authority. Tripoli. Libya. In Arabic version*

Gacia. E, Invers. O, Manzanera. M, Ballesteros. E, Romero. J. (2007) Impact of the brine from a desalination plants on a shallow seagrass (Posidonia oceanica) meadow, Journal of Estuarine, *Coastal and shelf Science***,** [online] v.72 (4), May, pp.579-590
Available at: http://www.sciencedirect.com/science/article/pii/S0272771406005221
[Accessed 24th July 2015]

Gwada. P. (2004) *An assessment of seagrass survival and Function in response to manipulations in sediment redox at Nyali Lagoon, Kenya. Report, Marine Ecological and Environmental Research Programme*, [online], February, pp.1-39
Available at: http://www.oceandocs.org/bitstream/handle/1834/1284/WIOMSAMARG-I200401PGWADA.pdf?sequence=1&isAllowed=y
[Accessed 24th July 2015]

Gude. V. (2016) Desalination and sustainability -An appraisal and current perspective. Water Research [online], v.89 (1), February, pp. 87-106.
Available at: http://www.sciencedirect.com/science/article/pii/S0043135415303390
[Accessed 24th July 2014]

General Electricity Company. (2014) *Libya Electricity Tariffs: Dynamic, Energy and water solution*, [online]
Available at: http://www.dynamic-ews.com/Tariffs/Electricity%20Tariffs/Libya.pdf
[Accessed 24th July 2014]

González. A, Urtiaga. A, Ibáñez. R and Ortiz. I. (2012) State of the art and review on the treatment technologies of water reverse osmosis concentrates, *Water Research* [online], v.46 (2). February, pp.267-283
Available at: http://www.sciencedirect.com/science/article/pii/S0043135411006440
[Accessed 24th July 2015]

Hamed. O. (2005) Overview of hybrid desalination systems — current status and future prospects, *Desalination*, [online], v.186 (3), December, pp. 207-214

Available at: http://www.sciencedirect.com/science/article/pii/S0011916405006934 [Accessed 24th July 2014]

Hu. Z. (2014) *Comparison of sustainability of technologies for water desalination*, [online], Master's Thesis in Chemical and Process Engineering, School of Technology, Lappeenranta University of Technology
Available at: https://core.ac.uk/download/pdf/39962109.pdf
[Accessed 24th July 2015]

Henthorne. L, Pankratz. T and Murphy. S. (2011) *The state of desalination 2011: IDA World Congress on Desalination and Water Reuse, Desalination: Sustainable Solutions for a Thirsty Planet*, [online], September.
Available at: http://desalination.edu.au/wp-content/uploads/2011/09/IDA-State-of-Desalination-2011.pdf
[Accessed 24th July 2014]

Hamed. O, Mustafa. G, BaMardouf. K and Al-Washmi. H. (2001) Prospects of improving energy consumption of the multi-stage flash distillation process, *Proceedings of the Fourth Annual Workshop on Water Conservation in the Kingdom of Saudi Arabia* [online], Dhahran, 23rd - 25th April,
Available at: https://www.researchgate.net/publication/242319364_PROSPECTS_OF_IMPROVING_ENERGY_CONSUMPTION_OF_THE_MULT-STAGE_FLASH_DISTILLATION_PROCESS1
[Accessed 24th July 2014]

Hoepner. T. (1999) A procedure for environmental impact assessments (EIA) for seawater desalination plants, *Desalination*, [online], v.124 (3), November, pp.1-12
Available at: http://www.sciencedirect.com/science/article/pii/S0011916499000831
[Accessed 24th July 2015]

http://www.water-technology.net/projects/al-khafji-solar-saline-water-reverse-osmosis-solar-swro-desalination-plant/

Hamieh. B, Beckman. J and Ybarra. M. (2001) Brackish and seawater desalination using a 20 ft^2 dewvaporation tower, *Desalination* , [online], v.140 (3), Novmber,pp.217-226,
Available at: http://www.sciencedirect.com/science/article/pii/S001191640100371X
[Accessed 24th July 2014]

Haddoud. D. (2013) interview by Ali El.hajaji. Marine Biology Research Centre. Libya. 3rd July.

Hamad. T, Agll. A, Hamad. Y and Sheffield. J. (2014) Solid waste as renewable source of energy: current and future possibility in Libya, *Case Studies in Thermal Engineering*, [online], v.4 (1), November, pp.144-152

Available at: http://www.sciencedirect.com/science/article/pii/S2214157X1400032X [Accessed 24th July 2015]

Hartog. C. (1970) *The Sea-Grasses of the World. Amsterdam*, London: North-Holland Publications Company, [online], pp.1-29
Available at: http://pdf.usaid.gov/pdf_docs/PNAAM467.pdf
[Accessed 24th July 2014]

Hillman. K, McComb. A and Walker. D.(1995) The distribution, biomass and primary production of the seagrass Halophila ovalis in the Swan/Canning Estuary, Western Australia, *Aquatic Botany*,[online], v.51 (2), July,pp.1-54
Available at: http://www.sciencedirect.com/science/article/pii/030437709500466D
[Accessed 24th July 2014]

Hiscock. K, Southward. A, Tittley. I, Hawkins. A. (2004) Effect of changing temperature on benthic marine life in Britain and Ireland, Aquatic Conservation: *Marine and Freshwater Ecosystems*, [online], v.14 (4), Jun, pp.333-362
Available at: http://onlinelibrary.wiley.com/doi/10.1002/aqc.628/pdf
[Accessed 24th July 2014]

Hargrave. B. (2005) *Environmental effects of Marine finfish Aquaculture*, Berlin: Springer.

Hair. J. Anderson. R. Tatham. L. Black. W. (1995) *Multivariate data analysis*. 4th ed. New Jersey: Prentice-Hall.

Howarth. R and Teal. J. (1979) Sulphate reduction in a New England salt marsh, *Journal of Limnology and Oceanography*,[online], v.24 (6), November, pp.999-1013
Available at: - http://onlinelibrary.wiley.com/doi/10.4319/lo.1979.24.6.0999/pdf
[Accessed 24th July 2014]

Hashim. A and Hajjaj. M. (2005) Impact of desalination plants fluid effluent on the integrity of seawater, with the Arabian Gulf in perspective, *Journal of Desalination and Environment***,** [online], v.182 (3), November, pp.373-393
Available at: http://www.sciencedirect.com/science/article/pii/S0011916405004534
[Accessed 24th July 2014]

Hsu. G, Hsia. C and Hsu. S. (2015) Effects of electrode settings on chlorine generation efficiency of electrolyzing seawater, *Food and Drug Analysis*, [online], v.23 (4), Decmber.pp.729-734.
Available at: http://www.sciencedirect.com/science/article/pii/S1021949815000915
[Accessed 24th July 2014]

Hajbi. F, Hammi. H and M'nif. A. (2010) Reuse of RO Desalination Plant Reject Brine, *Phase Equilibria and Diffusion,* [online], v.31 (4), August, pp. 341-347

Available at: http://link.springer.com/article/10.1007/s11669-010-9727-3
[Accessed 24th July 2015]

https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=+salt+price&isGalleryList=G

http://www.economist.com/node/15276675

International Monetary Fund. (2013) *Staff Country Reports: Libya. Report No (13). Washington. USA*, [online].
Available at: https://books.google.co.uk/books?id=lHkJ303fme8C&printsec=frontcover&source=gbs_ge_summary_r&cad=0#v=onepage&q&f=false
[Accessed 24th July 2015]

ICRC, (2012) *Water and habitat department: International Committee of the Red Cross*, Unpublished.

Invers. O, Romero J and Pe´rez. M (1997) Effects of pH on seagrass photosynthesis: a laboratory and field assessment. *Aquatic Botany*, [online], v.59 (4), December, pp.185-194
Available at: http://www.sciencedirect.com/science/article/pii/S0304377097000727
[Accessed 24th July 2014]

Irmak. S, Irmak. A, Jones. J, Howell. T, Jacobs. J, Allen. R and Hoogenboom. G. (2003) Predicting Daily Net Radiation Using Minimum Climatological Data, Irrigation and Drainage Engineer, [online], v.129 (4), August, pp.256-269
Available at: http://ascelibrary.org/doi/pdf/10.1061/(ASCE)0733-9437(2003)129:4(256)
[Accessed 24th July 2015]

Johnson. D, Lott. J and Sliepcevich. C. (1976) The exchange crystallization freeze desalination process, *Desalination*, [online], v.18 (3), June, pp.231-240
Available at: http://www.sciencedirect.com/science/article/pii/S0011916400841156
[Accessed 24th July 2014]

Johnson. D, Lott. J and Seliepcevich. C. (1976) The exchange crystallization freeze desalination process, *Desalination*, [online], v.18 (3). Pp. 231-240
Available at: http://www.sciencedirect.com/science/article/pii/S0011916400841156
[Accessed 24th July 2014]

Jirka. G. (2008) Improved Discharge Configurations for Brine Effluents from Desalination Plants, *Hydraulic Engineering*, [online], v.134 (1), January, pp.166-120
Available at: http://ascelibrary.org/doi/full/10.1061/(ASCE)0733-9429(2008)134%3A1(116)
[Accessed 24th July 2014]

Kepke. J, Foster. L, Gesca J and McCann. D. (2008) *Hold the salt: innovative treatment of RO concentrate,* [online], January, pp. 2619-2630
Available at: https://www.researchgate.net/publication/274226393_Hold_the_Salt_Innovative_Treatment_of_RO_Concentrate
[Accessed 24th July 2014]

Jack. J, Abdsalam. A and Khalifa. N. (2009) Assessment of dissolved oxygen in coastal waters of Benghazi, Libya, *Journal of Black Sea/Mediterranean Environment*, [online], v.15 (3), October, pp. 135-156,
Available at: http://edc-connection.ebscohost.com/c/articles/52249539/assesment-dissolved-oxygen-coastal-waters-benghazi-libya
[Accessed 24th July 2014]

Joyce. C, Vina. C and Metcalfe. D. (2005) Biotic variation in coastal water bodies in Sussex, England: Implication for saline lagoons, Journal of Estuarine, *Coastal and Shelf Science***,** [online], v.65 (4), December, pp. 633-644
Available at: http://www.sciencedirect.com/science/article/pii/S027277140500243X
[Accessed 24th July 2014]

Joseph. A and Sharma. S. (2012) *The IIT Foundation Series - Physics*, 2nd ed, Dorling Kindersley, India.

Khawaji. A, Kutubkhanah. I and Wie. J. (2008) Advances in seawater desalination technologies, *Desalination*, [online], v.221 (3), March, pp.47-69
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407006789
[Accessed 24th July 2014]

Krishna. H. (2004) *Introduction to Desalination Technologies. Texas Water Development Board*, [online]
Available at: http://www.twdb.texas.gov/publications/reports/numbered_reports/doc/r363/c1.pdf
[Accessed 24th July 2014]

Khordagui, H. (2013). *Assessment of potential cumulative environmental impacts of desalination plants around the Mediterranean Sea. SWIM Final report, Activity 1.3.2.1.*
Available at: http://www.swim-sm.eu/files/Environmental_Impacts_of_Desalination.pdf
[Accessed 24th July 2014]

Kershman. S. (2001) 25 years of experience in operating thermal desalination plants, *Desalination*, [online], v.136 (3), May, pp.141-145
Available at: http://www.sciencedirect.com/science/article/pii/S001191640100176X

[Accessed 24th July 2014]

Khawaji. A and Wie. J. (1994) Potabilization of desalinated water at Madinat Yanbu Al-Sinaiyah, *Desalination*, [online], v.98 (3), September, pp.135-146
Available at: http://www.sciencedirect.com/science/article/pii/0011916494001383
[Accessed 24th July 2014]

Kalogirou. S. (2005) Seawater desalination using renewable energy sources, *Progress in Energy and Combustion Science*, [online], v.31 (3), March, pp.242-281
Available at: http://www.sciencedirect.com/science/article/pii/S0360128505000146
[Accessed 24th July 2014]

Karagiannis. I and Soldatos. P. (2008) Water desalination cost literature: review and assessment, *Desalination*, [online], v.223 (3), March, pp.448-456.
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407008843
[Accessed 24th July 2014]

Katzir. L, Volkmann.Y, Daltrophe. N, Korngold. E, Mesalem. R, Oren. Y and Gilron. J. (2010) WAIV-Wind aided intensified evaporation for brine volume reduction and generating mineral byproducts, *Desalination and Water Treatment*, [online], v.13 (3), Jun, pp.63-74
Available at: http://www.tandfonline.com/doi/abs/10.5004/dwt.2010.772
[Accessed 24th July 2014]

Khalil. A and Asheibi. A. (2015) The Chances and Challenges for Renewable Energy in Libya. *Proceedings in the 4th International Conference on Renewable Energy Research and Applications*, [online], Palermo, Italy,22-25 November, pp 1-6
Available at: https://www.researchgate.net/profile/Ashraf_Khalil13/publication/283722527_The_Chances_and_Challenges_for_Renewable_Energy_in_Libya/links/5853966208aef7d030a52abd/The-Chances-and-Challenges-for-Renewable-Energy-in-Libya.pdf
[Accessed 24th July 2015]

Kuwairi. A. (2006) Water mining: the Great Man-made River, Libya, *Proceedings of the Institution of Civil Engineers - Civil Engineering*, [online], Libya, 1st May,v.159 (5), pp.39-43
Available at: http://www.icevirtuallibrary.com/doi/pdf/10.1680/cien.2006.159.5.39
[Accessed 24th July 2015]

Khalafallah. A, Geneid .Y, Shaetaey. S and Shaaban. B. (2013) Responses of the seagrass Halodule uninervis (Forssk.) Aschers to hypersaline conditions, *Journal of Aquatic Research-Egypt*, [online], v.39 (3), October, pp.167-176
Available at: http://www.sciencedirect.com/science/article/pii/S168742851300109X
[Accessed 24th July 2014]

Korovessis. N and Lekkas. T. (2009) Solar saltworks Wetland function, *Global nest* [online], v.11 (1), October, pp. 49-57.
Available at: http://journal.gnest.org/sites/default/files/Journal%20Papers/49-57_575_Korovessis.pdf
[Accessed 24th July 2015]

Kavakli. Z, Tsirtsis. G, Korovessis. N, Karydis. M. (2006) A comparative analysis of the ecological systems of two Greek seasonal saltworks (Mesolonghi and Kalloni): Implications for salt production, *Proceedings of the 1st International Conference on the Ecological Importance of Solar Saltworks (CEISSA 06)*, [online], Santorini Island, Greece, 20-22, October, pp.95-102.
Available at: http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=7858
[Accessed 24th July 2015]

Kasedde. H. (2013) *Characterization of Raw Materials for salt Extraction from Lake Katwe, Uganda*, 1-35. [online] MSc. Thesis, KTH, Royal Institute of Technology, Stockholm University, Sweden.
Available at: https://www.diva-portal.org/smash/get/diva2:667784/FULLTEXT01.pdf
[Accessed 24th July 2015]

Lattemann. S and Höpner. T. (2008) Environmental impact and impact assessment of seawater desalination, *Desalination*, [online], v.220 (3), March.pp.1-15
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407006005
[Accessed 24th July 2015]

Lattemann. S. (2010) *Development of an environmental impact assessment and decision support system for seawater desalination plants*, [online], Ph. D, thesis, Delft University of Technology and of the Academic Board of the UNESCO-IHE Institute for Water Education, Salzgitter, Germany
Available at: https://books.google.co.uk/books?hl=en&lr=&id=2kXLBQAAQBAJ&oi=fnd&pg=PP1&dq=Development+of+an+environmental+impact+assessment+and+decision+support+system+for+seawater+desalination+plants&ots=vWhKRzwx7K&sig=i0dXo8hPno2NdPiPsNWPR0JvIiA#v=onepage&q=Development%20of%20an%20environmental%20impact%20assessment%20and%20decision%20support%20system%20for%20seawater%20desalination%20plants&f=false
[Accessed 24th July 2017]

Lenntech, (1998) *Reverse Osmosis Desalination Process*, [online image]
Available at: http://www.lenntech.com/processes/desalination/reverse-osmosis/general/reverse-osmosis-desalination-process.htm
[Accessed 24th July 2014]

Leong. J, Tan. J, Charrois. J and Ladweig. B. (2014) Review of high recovery concentrate management options, *Desalination and Water Treatment*, [online], v.52 (42), August, pp.7609-7627

Available at: http://www.tandfonline.com/doi/abs/10.1080/19443994.2013.834273 [Accessed 24th July 2014]

Lu. H, Walton. J and Hein. H. (2002) *Thermal Desalination using MEMS and Salinity-Gradient Solar Pond Technology, Desalination Research and Development Program Report No. 80, University of Texas at El Paso El Paso, Texas [online]*, Aguste. pp.1-40
Available at: https://www.usbr.gov/research/AWT/reportpdfs/report080.pdf
[Accessed 24th July 2014]

Latteman. S. (2010) *Development of an Environmental Impact Assessment and Decision Support System for Seawater Desalination Plant*, [online] Ph.D. thesis. Delft University of Technology
Available at: https://books.google.co.uk/
[Accessed 24th July 2014]

Latorre. M. (2005) Environmental impact of brine disposal on Posidonia seagrasses, *Desalination*, [online], v.182 (3), November, pp 517–524.
Available at: http://www.sciencedirect.com/science/article/pii/S0011916405004662
[Accessed 24th July 2014]

Ladewig. B and Asquith. B. (2011) *Desalination Concentrate Management*. Australia. Springer

Les. E. (2015) *Reducing Corrosion and potential Boiler Failure with Superior Iron: Transport Technology*, [online], pp.1-37
Available at: http://www.nace-jubail.org/meetings/nace_jubail%20gewpt1.pdf
[Accessed 24th July 2014]

Lozides. L. (2015) The Cost of Environmental and Social Sustainability of Desalination, *Marine Pollution Chemistry*, [online], pp. 175-189
Available at: http://132.68.226.240/english/pdf/IDS/96.pdf
[Accessed 24th July 2014]

Lattemann. S. (2005) *Potential Impacts of Seawater Desalination*, [online], Available at: http://www.paua.de/Impacts.htm
[Accessed 24th July 2014]

Laspidou. C, Hadjibiros. K and Gialis. S. (2010) Minimizing the environmental impact of sea brine disposal by coupling desalination plants with solar saltworks: A case study for Greece, *Journal of Water*, [online], v.2 (1), February, pp.75-84
Available at: http://www.mdpi.com/2073-4441/2/1/75,
[Accessed 24th July 2014]

Laˇcnjevaca. U, Jovi´ca. B, Gaji´c-Krstaji. Lj, Kovaˇc. J, Jovi´ca. V, Krstaji´c. N. (2013) Ti substrate coated with composite Cr–MoO2 coatings as highly selective cathode materials in hypochlorite production, *Electrochimica Acta*. [online], v.96 (1), April, pp. 34-42.

Available at: http://www.sciencedirect.com/science/article/pii/S0013468613003319 [Accessed 24th July 2014]

Ladewig. B and Asquith. B. (2012) Desalination Concentrate Management: Evaporation Ponds Industrial Chemistry and Chemical Engineering, Berlin Heidelberg, Springer.

Milano. M, Ruelland. D, Fernandez. S, Dezetter. A, Fabre. J, Servat. E, Fritsch.J, Bardin. S and Thivet. G. (2013) Current state of Mediterranean water resources and future trends under climatic and anthropogenic changes, *Hydrological Sciences*, [online], v.58 (3), March, pp.498-518
Available at: http://www.tandfonline.com/doi/full/10.1080/02626667.2013.774458 [Accessed 24th July 2017]

Medeazza. G. (2005) "Direct" and socially-induced environmental impacts of desalination, *Desalination*, [online], v.185 (3), November, pp. 57-70
Available at: http://www.sciencedirect.com/science/article/pii/S0011916405006089 [Accessed 24th July 2017]

Mezher. T, Abbas. H and Khaled. A. (2011) Techno-economic assessment and environmental impacts of desalination technologies, *Desalination*, [online], v. 266 (3), January, pp. 263-273.
Available at: http://www.sciencedirect.com/science/article/pii/S0011916410006296 [Accessed 24th July 2014]

Miller. J. (2003) Review of Water Resources and Desalination Technologies, Sandia National Laboratories. California. USA, [online], March, pp. 1-49
Available at: http://prod.sandia.gov/techlib/access-control.cgi/2003/030800.pdf [Accessed 24th July 2014]

Mahdavi. M, Mahvi. A and Nasseri. S. (2011) Application of Freezing to the Desalination of Saline Water, *Arabian Journal for Science and Engineering*, [online], v.36 (7), November, pp.1171-1177.
Available at: http://link.springer.com/article/10.1007/s13369-011-0115-z [Accessed 24th July 2014]

Mickley. M. (2006) *Membrane Concentrate Disposal: Practices and Regulation, Desalination and Water Purification Research and Development Program*: Report No. 123, 2nd edn. U.S. Department of the Interior, Bureau of Reclamation. Denver. [online], April, pp. 1-303
Available at: https://www.usbr.gov/research/AWT/reportpdfs/report123.pdf [Accessed 24th July 2015]

Masnoon. S & Glucina. K. (2011) *Desalination: Brine and Residual Management: Project WWIR N°RI024:Réf. : RI024_PEP_KG/sm/18695: Global Water Research Coalition-Report* [online], October, pp.2-91
Available at: http://www.waterrf.org/resources/Lists/SpecialReports/Attachments/2/GWRC_State_of_Science_Report_on_Brine_and_Residual_Management.pdf
[Accessed 24th July 2014]

Mickley. M. (2001) Membrane concentrate disposal: Practices and regulation. Desalination and Water Purification Research and Development Program Report No. 69, [online], September, pp. 1-252
Available at: http://www.usbr.gov/research/AWT/reportpdfs/report069.pdf
[Accessed 24th July 2014]

Mickley, M. C. (2009) *Treatment of Concentrate, Desalination and Water Purification Research and Development Program Report N. 155, U.S. Department of Interior Bureau of Reclamation, Denver, Colo. [online], May, pp.1-155*
Available at: https://www.usbr.gov/research/AWT/reportpdfs/report155.pdf
[Accessed 24th July 2014]

Mohamed. A, Maraqa. M, Al Handhaly. J. (2005) Impact of land disposal of reject brine from desalination plants on soil and groundwater, *Desalination,* [online], v.182 (3), November, pp. 411-433
Available at: http://www.sciencedirect.com/science/article/pii/S001191640500456X
[Accessed 24th July 2014]

Morillo. J, Usero. J, Rosado. D, El Bakouri. H, Riaza. A and Bernaola. F. (2014) Comparative study of brine management technologies for desalination plants, *Desalination,* [online], v.336 (1), March, pp.32-49
Available at: http://www.sciencedirect.com/science/article/pii/S0011916414000071
[Accessed 24th July 2014]

Mackey. E and Seacord. T. (2008) *Regional Solutions to Concentrate Management, Water Reuse Foundation Project No. WRF-02-006d-01, Water Reuse Foundation, Alexandria VA, [online], pp.1-129*
Available at: http://www.waterboards.ca.gov/water_issues/programs/grants_loans/water_recycling/research/02_006d_01.pdf
[Accessed 24th July 2014]

MacDonald. A, Bonsor. H, Dochartaigh. B and Taylor. R. (2012) Quantitative maps of groundwater resources in Africa, *Environmental Research Letters,*[online], v.7 (2), April, pp.1-7
Available at: http://iopscience.iop.org/article/10.1088/1748-9326/7/2/024009/meta
[Accessed 24th July 2014]

Mohamed. A, Al-Habaibeh. A, Abdo. H and Elabar. S. (2015) Towards exporting renewable energy from MENA region to Europe: An investigation into domestic

energy use and householders' energy behaviour in Libya, *Applied Energy*, [online], v.146 (15), May, pp.247-262.
Available at: http://www.sciencedirect.com/science/article/pii/S0306261915001750
[Accessed 24th July 2015]

Mohamed. S. (2013) Interview by Ali Elhajaji. Tripoli. Libya. 13 September 2013
Middle East business intelligence. (2010) The Great Man-made River project: MEED project, [online]
Available at: https://www.meed.com/Journals/1/Files/2011/12/11/Sample%20Chapter.pdf
[Accessed 24th July 2015]

Moreno. A, Torquemada. Y and Lizaso. J. (2014) Salinity fluctuation of the brine discharge affects growth and survival of the seagrass Cymodocea nodosa, *Journal of Marine Pollution Bulletin*, [online], v.81 (1), April, pp 61-60
Available at: http://www.sciencedirect.com/science/article/pii/S0025326X14001155
[Accessed 24th July 2014]

Marsh. J, Dennison. W and Alberte. R. (1986) Effects of temperature on photosynthesis and respiration in eelgrass (Zostera marina L.), *Journal of Experimental Marine Biology and Ecology*, [online], v.101 (3), November, pp.257-267
Available at: http://www.sciencedirect.com/science/article/pii/0022098186902674#
[Accessed 24th July 2014]

Mabrook. B. (1994) Environmental impact of waste brine disposal of desalination plants, Red Sea, Egypt. *Desalination*, [online], v.97 (3), August, pp.453-465.
Available at: http://www.sciencedirect.com/science/article/pii/0011916494001081
[Accessed 24th July 2014]

Mazini. M, Yazdizadeh. A and Ramezani. M. (2014) Dynamic modelling of multi-effect desalination with thermal vapour compressor plant, *Journal of Desalination*, [online], v.353 (1), November, pp.98-108
Available at: http://www.sciencedirect.com/science/article/pii/S0011916414004895
[Accessed 24th July 2014]

Malcolm. F and Lancaster. J. (2013) *Analysis of Marine Ecology Monitoring Plan Data from the Robin Rigg Offshore Wind Farm, Scotland (Operational Year 3), Report Nr: 1029455*, [online], September, pp.1-58
Available at: http://www.gov.scot/Resource/0046/00463655.pdf
[Accessed 24th July 2014]

Murphy. S. (2014) *Global water watch program: More information about parameters: Auburn University*, [online],
Available at: http://www.globalwaterwatch.org/GWW/GWWeng/GWWhardnessEng.aspx

[Accessed 24th July 2014]

Morenoa. A, McDonald. A, Shermand. T, Sánchez-Lizasoa. J, Jr. K and Cebrian. J. (2014) Short-term impacts of salinity pulses on ionic ratios of the seagrasses Thalassia testudinum and Halodule wrightii, *Journal of Aquatic Botany*, [online], v.120 (2), pp.315-321
Available at: http://www.sciencedirect.com/science/article/pii/S030437701400151X
[Accessed 24th July 2014]

Manzanera. M, Pe´rez. M and Romero. J (1998) Seagrass mortality due to oversedimentation: an experimental approach, *Journal of Coastal Conservation*, [online], v.4(1), December, pp.67-70
Available at: https://link.springer.com/article/10.1007/BF02806491
[Accessed 24th July 2014]

Mottaleb. S. (2013) *Molecular basis of salt tolerance in Physcomitrella Patens model plant: potassium homeostasis and physiological roles of chx transporters*, PhD thesis: Universidad Politécnica de Madrid [online], November, pp.1-164
Available at: http://oa.upm.es/21428/1/SHADY_ABDEL_MOTTALEB.pdf
[Accessed 24th July 2014]

Marie. Z. (2010) *Thermal Desalination: Structural Optimization and Integration in Clean Power and Water*, MSc thesis, Massachusetts Institute of Technology. Dept. of Mechanical Engineering, [online], June, pp. 1-144
Available at: http://dspace.mit.edu/handle/1721.1/74955
[Accessed 24th July 2014]

Morrision. G and Greening. H. (2015) *Seagrass. Chapter 4*, [online], pp. 63-103, Available at: http://pubs.usgs.gov/circ/1348/pdf/Chapter%204_63-104.pdf
[Accessed 24th July 2014]

Montefalcone. M, Albertelli. G, Bianchi. C, Mariani. M and Morri. C. (2005) A new synthetic index and a protocol for monitoring the status of Posidonia oceanica meadows: a case study at Sanremo (Ligurian Sea, NW Mediterranean), Journal of Aquatic Conservation: *Marine and Freshwater Ecosystems*, [online], v.16 (1), pp.29-42,
Available at: http://onlinelibrary.wiley.com/doi/10.1002/aqc.688/pdf
[Accessed 24th July 2014]

Murthy. P, Venkatesan. R, Nair. K, Inbakandan. D, Jahan. S, Peter. D and Ravindran. M. (2005) Evaluation of sodium hypochlorite for fouling control in plate heat exchangers for seawater application, *International Biodeterioration & Biodegradation.* [online], v. 55 (3), April, pp.161-170
Available at: http://www.sciencedirect.com/science/article/pii/S0964830504001350
[Accessed 24th July 2014]

Moosvi. J. (2006) Ecological importance of solar saltworks, *Proceedings of the 1st International Conference on the Ecological Importance of Solar Saltwork*s, [online], Santorini Island, Greece,20-22, October, pp. 243-248.
Available at: http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=7878
[Accessed 24th July 2015]

Mohammed. O. (2003) *The Chemical Complex utilizes Libyan natural resources of brine: General Company for Chemical Industries (Libya): 2-GCCI.* [Report in Arabic version]

Madkour. F and Gaballah. M. (2012) Hypersaline Environments. Microbiology and Biogeochemistry, Oceanologia. [online], v.54 (4), November, pp.687-700.
Available at: http://www.sciencedirect.com/science/article/pii/S0078323412500321
[Accessed 24th July 2015]

Muftah.T, (2014) *Sabratha University: Department of Environmental engineering: laboratory documents, Libya* [in Arabic version].

National Research Council. (2008) *Desalination: A National Perspective*. Washington, D.C, National Academies Press.
Available at: https://books.google.co.uk/books?hl=en&lr=&id=L-pTAgAAQBAJ&oi=fnd&pg=PT15&dq=National+Research+Council+(NRC)++desalination&ots=SwG_I48bZB&sig=Kk84MBzMt-5zESgEYz3Alz01zU0#v=onepage&q=National%20Research%20Council%20(NRC)%20%20desalination&f=false
[Accessed 24th July 2017]

Nait. S. (2015) *ENPI-SEIS project: Country Report – LIBYA: European Environment Agency* [online], March, pp.1-16
Available at: http://www.eea.europa.eu/
[Accessed 24th July 2014]

Neilly. A, Jegatheesan.V and Shu. L. (2009) Evaluating the potential for zero discharge from reverse osmosis desalination using integrated processes – A review, *Desalination and water treatment*, [online],v.11 (3), August, pp. 58-65.
Available at: http://www.tandfonline.com/doi/abs/10.5004/dwt.2009.843
[Accessed 24th July 2014]

National Oil Corporation. (2014) A brief about the National Oil Corporation, [online]
Available at: https://noc.ly/index.php/en/about-us-2
[Accessed 24th July 2015]

Naser. H. (2013) Effects of Multi-Stage Flash and Reverse Osmosis Desalinations on Benthic Assemblages in Bahrain, Arabian Gulf, *Journal of Environmental Protection*, [online], v.4 (2), February, pp. 180-187

Available at: http://www.scirp.org/journal/PaperInformation.aspx?PaperID=28320#.VLGOGzGsXO4 [Dec.21, 2014].
[Accessed 24th July 2014]

Naser. H. (2014) *Marine Ecosystem Diversity in the Arabian Gulf: Threats and Conservation. In: Grillo. O, Biodiversity - The Dynamic Balance of the Planet, PhD. Oscar Grillo (Ed), InTech, DOI: 10.5772/57425*, [online], May, pp.297-328
Available at: http://www.intechopen.com/books/biodiversity-the-dynamic-balance-of-the-planet/marine-ecosystem-diversity-in-the-arabian-gulf-threats-and-conservation
[Accessed 24th July 2014]

Niu. X, Bressan. R, Hasegawa. P and Pardo. J. (1995) Ion Homeostasis in NaCl Stress Environments, *Journal of Plant Physiology*, [online], v.109 (3),November, pp.735-742.
Available at: - http://www.ncbi.nlm.nih.gov/pmc/articles/PMC161372/
[Accessed 24th July 2014]

North. G, Schmandt. J and Clarkson. J. (1995) *The impact of global warming on Texas: A Report of the Task Force on Climate Change in Texas*. USA. University of Texas Press.

Nylén. L. (2008) *Influence of the electrolyte on the electrode reactions in the chlorate process*. [online], PhD. Thesis, Royal Institute of Technology, University in Stockholm, Sweden.pp.1-55.
Available at: http://www.diva-portal.org/smash/get/diva2:13397/fulltext01.pdf
[Accessed 24th July 2014]

Nicot. J, Gross. B, Walden. S and Baier. R. (2009) *Self-Sealing Evaporation Ponds for Desalination Facilities in Texas*; *Contract No. 2005-483-027; Texas Water Development Board*, [online], Austin, January, pp. 1-225
Available at: http://www.twdb.texas.gov/innovativewater/desal/doc/SSEP_FinalReport_Rev1.pdf [Accessed 24th July 2015]

Ozair. G and Al-Shangiti. M. (2013) Best practices in the management of disinfection by-products & their formation potential, *Proceedings of the International Desalination Association World Congress on Desalination and Water Reuse*, [online], Tianjin, China, pp.1-18
Available at : http://www.academia.edu/18069333/BEST_PRACTICES_IN_THE_MANAGEMENT_OF_DISINFECTION_BY-PRODUCTS_and_THEIR_FORMATION_POTENTIAL
[Accessed 24th July 2014]

Oil and Water Supplies Limited (2006) *Water Treatment Chemicals: PRO-TEK SB 101*, [online].
Available at: http://www.owsupplies.biz/water/tcd.html

[Accessed 24th July 2014]

Owens. N. (2009) *What is ocean acidification*?, [online]
Available at: http://www.rgs.org/ourwork/Schools/Geography+in+the+news/Ask+the+experts/ocean+acidification.htm
[Accessed 24th July 2014]

Olivier. L and Kovacik. J. (2006) The 'Briquetage de la Seille' (Lorraine, France): proto-industrial salt production in the European Iron Age, *Antiquity*, [online], v. 80 (309), September, pp.558-566.
Available at: http://journals.cambridge.org/action/displayAbstract?fromPage=online&aid=9436994
[Accessed 24th July 2015]

Oren. A, Sørensen. K, Canfield. D, Teske. A, Ionescu. D, Lipski. A and Altendorf. K. (2009) Microbial communities and processes within a hypersaline gypsum crust in a saltern evaporation pond (Eilat, Israel), *Hydrobiologia,* [online], v.626 (1), june.pp.15-26
Available at: http://link.springer.com/article/10.1007/s10750-009-9734-8
[Accessed 24th July 2015]

Pinto. F and Marques. R. (2017) Desalination projects economic feasibility: A standardization of cost determinants, *Renewable and Sustainable Energy Reviews*, [online], v.78 (1), October, pp.904-915
Available at: http://www.sciencedirect.com/science/article/pii/S1364032117306585
[Accessed 24th July 2017]

Plumley. J. (2005) *ABB: Improving power plant efficiency using analytical instrumentation*, [online], January
Available at: http://www.abb.com/cawp/seitp202/f95b7920b6f64682c1256f8d0055b672.aspx
[Accessed 24th July 2015]

Purnalna. A, Al-barwani. H, Al-Lawati. M. (2003) Modelling dispersion of brine waste discharge from a coastal desalination plant, *Desalination,* [online], v.155 (1), May, pp.41-47
Available at: http://www.sciencedirect.com/science/article/pii/S0011916403002376
[Accessed 24th July 2014]

Palomar. P and Losada. I. (2010) Desalination in Spain: Recent developments and recommendations, *Desalination,* [online], v.225 (3), May, pp.97-106
Available at: http://www.sciencedirect.com/science/article/pii/S0011916410000305
[Accessed 24th July 2014]

Parker. B. (2002) Planning Analysis: Calculating Growth Rates, [online] Available at: http://pages.uoregon.edu/rgp/PPPM613/class8a.htm [Accessed 24th July 2015]

Pagès. J, Pérez. M and Romero. J. (2010) Sensitivity of the seagrass Cymodocea nodosa to hypersaline conditions: A microcosm approach, *Journal of Experimental Marine Biology and Ecology*, [online], v. 386 (2), April, pp. 34-38 Available at: http://www.sciencedirect.com/science/article/pii/S0022098110000729 [Accessed 24th July 2014]

Parry. G. (1960) The development of salinity tolerance in the salmon, salmon salmo (L) and some related species, Exp. *Biol*, [online], v. 37 (1), February, pp. 425–434. Available at: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.562.2654&rep=rep1&type=pdf [Accessed 24th July 2014]

Pallant. J. (2010) *SPSS Survival Manual: A step by step guide to data analysis using SPSS*. 4th ed, London. UK: McGraw Hill

Placenti. F, Schroeder. K, Bonanno. A, Zgozi. S, Sprovieri. M, Borghini. M, Rumolo. P, Gerrati. G, Bonnomo. S, Genovese. S, Basilone. G, Haddoud. D, Patti. B, El-turki. A, Hamza. M, Mazzola. S. (2013) Water mass and nutrient distribution in the Gulf of Syrte and between Sicily and Libya, *Journal of Marine Systems*, [online], v.122 (1) July, pp. 36-46 Available at: http://www.sciencedirect.com/science/article/pii/S092479631300081X [Accessed 24th July 2014]

Penman. L. (1948) Natural evaporation from open water, bare soil, and grass. *Mathematical and Physical*, [online], v.193 (1032), April, pp.120-145 Available at: http://www.jstor.org/stable/98151?origin=JSTOR-pdf&seq=1#page_scan_tab_contents [Accessed 24th July 2015]

Qdais. H. (2008) Environmental impacts of the mega desalination project: the Red–Dead Sea conveyor. *Desalination*, [online], v.220 (3), March, pp.16-23. Available at: http://www.sciencedirect.com/science/article/pii/S0011916407006017 [Accessed 24th July 2014]

Rahimi. B and Chua. H. (2017) *Low Grade Heat Driven Multi-Effect Distillation and Desalination*. Oxford. UK: Elsevier

International Desalination Association. (2017) *Desalination by the Numbers*, [online], Available at: http://idadesal.org/desalination-101/desalination-by-the-numbers/ [Accessed 24th July 2014]

Raluy. G, Serra. L and Uche. J. (2006) Life cycle assessment of MSF, MED and RO desalination technologies, *Energy*, [online], v.31 (13), October, pp.2361-2372
Available at: http://www.sciencedirect.com/science/article/pii/S0360544206000442
[Accessed 24th July 2014]

Rice. W and Chau. D. (1997) Freeze desalination using hydraulic refrigerant compressors, *Desalination*, [online], v.109 (2), May, pp.157-164
Available at: http://www.sciencedirect.com/science/article/pii/S0011916497000611
[Accessed 24th July 2014]

Reimold. R, Loland-McLaughlin. G, and Bloetscher. F. (1996) An innovative opportunity for water reuse. *Florida water resources*, [online], July, 26-30
Available at: www.fwrj.com/articles/9607.pdf
[Accessed 24th July 2014]

Ruiz. J. and Romero. J. (2001) Effects of in situ experimental shading on the Mediterranean seagrass Posidonia oceanica, *Marine ecology*, [online], v.215 (1), March, pp. 107– 120.
Available at: http://www.int-res.com/articles/meps/215/m215p107.pdf
[Accessed 24th July 2014]

Royal Society (2005) Ocean acidification due to increasing atmospheric carbon dioxide, Policy Document 12/05, London: Clyvedon Press Ltd
[Accessed 24th July 2014]

Rasul. N and Stewart. I. (2015) *The Red Sea: The Formation, Morphology, Oceanography and Environment of a Young Ocean Basin*, Berlin

Ruíz. J, Guirao. L and Gil. J. (2009) Responses of the Mediterranean seagrass Posidonia oceanica to in situ simulated salinity increase, *Journal of Botanica Marina*, [online], v.52 (5), November, pp. 459–470.
Available at: https://www.degruyter.com/view/j/bot.2009.52.issue-5/bot.2009.051/bot.2009.051.xml
[Accessed 24th July 2014]

Roberts. D, Johnston. E and Knott. N. (2010) Impacts of desalination plant discharges on the marine environment: A critical review of published studies, *Journal of Desalination*, [online], v.44 (18), October, pp.5117-5128
Available at: http://www.sciencedirect.com/science/article/pii/S0043135410002903
[Accessed 24th July 2014]

Rabiu. A, Akinnigbagbe. E, Imo. O, Imhansoloeva. M, Ibitola. P, Faleye. R and Shonde. O. (2011) Textural Characteristics of Bottom Sediments in Parts of the Lagos Atlantic/Seabed Coastal Waters, *Journal of Life and Physical Sciences*, [online], vol.4 (1), September ,pp.64-73,
Available at: http://www.actasatech.com/index.php?q=journal.view.126
[Accessed 24th July 2014]

Roux. J, Nada. N, Khan. M and Croué. J. (2015) Tracing disinfection byproducts in full-scale desalination plants, *Desalination*. [online], v.359 (1), March, pp.141-148
Available at: http://www.sciencedirect.com/science/article/pii/S0011916414006821
[Accessed 24th July 2014]

Ronco. C and Mishkin. G. (2007) *Disinfection by Sodium Hypochlorite: Dialysis Applications*, Karger AG: Basel, Switzerland

Rivera. S and Matousek. R. (2015) *Overview: Chapter 1: AWWA manual: on-site generation of hypochlorite*, American Water Works Association. [online]
Available at: http://www.awwa.org/portals/0/files/publications/images/m65excerpt.pdf
[Accessed 24th July 2014]

Rabah. M, Nassif. N, and Azim. A. (1991) Electrochemical wear of graphite anodes during electrolysis of brine, *Carbon*. [online], v.29 (2), pp.165-171,
Available at: http://www.sciencedirect.com/science/article/pii/000862239190066R
[Accessed 24th July 2014]

Ravizky. A and Nadav. N. (2007) Salt production by the evaporation of SWRO brine in Eilat: a success story, Desalination, [online], v.205 (3), February, pp.374-379.
Available at: http://www.sciencedirect.com/science/article/pii/S0011916406013919
[Accessed 24th July 2015]

Rodríguez. F, Santiago. D, Suárez. N, Méndez. J and Veza. J (2012) Comparison of evaporation rates for seawater and brine from reverse osmosis in traditional salt works: empirical correlations, *Water Science and Technology: Water Supply*, [online], v.12 (2), December, pp. 234 - 240
Available at: http://ws.iwaponline.com/content/12/2/234
[Accessed 24th July 2015].

Sadeg. S and Karahanoðlu. N. (2001) Numerical assessment of seawater intrusion in the Tripoli region, Libya, *Environmental Geology*, [online], v.40 (9), pp.1151-1168
Available at: https://link.springer.com/article/10.1007/s002540100317
[Accessed 24th July 2014]

Saleh. I. (2006) *Prospects of renewable energy in Libya, International Symposium on Solar Physics and Solar Eclipses (SPSE),* [online]
Available at: http://www.google.co.uk/url?sa=t&rct=j&q=&esrc=s&source=web&cd=4&cad=rja&uact=8&ved=0ahUKEwje_9zSiPTWAhVJPBoKHQIEDkAQFgg8MAM&url

=http%3A%2F%2Fdata.irsol.ch%2Fspse%2Fspse-download.php%3Fpid%3D20&usg=AOvVaw0ag5LohcH3yX_42Ud7Cdst
[Accessed 24th July 2014]

Sekaran. U and Bougie. R. (2009) *Research Methods for Business: A Skill Building Approach (5th Edition)*, John Wiley & Sons Ltd, UK.

Shatat. M and Riffat. S. (2012) Water desalination technologies utilizing conventional and renewable energy sources, *Low-Carbon Technologies,* [online], v.9 (1), February. pp. 1-19.
Available at: https://academic.oup.com/ijlct/article/9/1/1/663897/Water-desalination-technologies-utilizing
[Accessed 24th July 2014]

Saidur. R, Elcevvadi. E, Mekhilef. S, Safari. A, Mohammed. H. (2011) An overview of different distillation methods for small scale applications, *Renewable and Sustainable Energy Reviews,* [online], v.15 (9), December, pp.4756-4762
Available at: http://www.sciencedirect.com/science/article/pii/S1364032111003224
[Accessed 24th July 2014]

Spiegler. K. (1977) *Salt water purification*. 2nd ed. New York. John Wiley and Sons.

Schenkeveld. M, Morris. R, Budding. B, Helmer. J and Innanen. S. (2004) *Seawater and Brackish Water Desalination in the Middle East, North Africa and Central Asia — A Review of Key issues and Experience in Six Countries (Algeria, Tunisia, Jordan, Uzbekistan, Malta, Cyprus),*World Bank, [online], December, pp.1-125
Available at: http://www.worldbank.org/watsan/bnwp
[Accessed 24th July 2014]

Sujay. K. (2012) *A Study of Retail Trade with special reference to Grocery Trade in Kolhapur city*, [online], Ph.D. thesis, Symbiosis International University, India
Available at: http://shodhganga.inflibnet.ac.in/handle/10603/15089
[Accessed 24th July 2017]

Sharon. H and Reddy. K. (2015) A review of solar energy driven desalination technologies, *Renewable and Sustainable Energy Reviews*, [online], v.41 (1), January, pp.1080-1118
Available at: http://www.sciencedirect.com/science/article/pii/S1364032114007758
[Accessed 24th July 2014]

SolarSpring. (2016) *Potable water for people process and wastewater treatment scientific investigations: Membrane Distillation*, [online image]
Available at: http://www.solarspring.de/index.php?id=7
[Accessed 24th July 2014]

Spiegler. K and Laird. A. (1980) *Principles of Desalination*: Pt.B, 2nd . New York: Academic Press.

Samee. M, Mirza. U, Majeed. T and Ahmad. N. (2007) Design and performance of a simple single basin solar still, *Renewable and Sustainable Energy Reviews,* [online],v.11 (3), April,pp.543-549
Available at: http://www.sciencedirect.com/science/article/pii/S1364032105000481
[Accessed 24th July 2014]

Svensson. M. (2005) *Desalination and the Environment: Options and considerations for brine disposal in inland and coastal locations: Department of Biometry and Engineering: Swedish University of Agricultural Sciences* [online], September, pp. 1-55
Available at: http://ex-epsilon.slu.se/805/1/exjobb_05_02.pdf
[Accessed 24th July 2014]

Sethi. S, Xu. P and Drewes. J (2007) New Desalination Configurations and Technologies for Recovery Increase and Concentrate Minimization. *Desalination, Municipal water, World Environmental and Water Resources Congress* [online], pp. 1-9.
Available at: http://dx.doi.org/10.1061/40927(243)450
[Accessed 24th July 2014]

Sethi. S, Walker. S, Drewes. J & Xu. P. (2006) Existing & Emerging Concentrate Minimization & Disposal Practices for Membrane Systems, *Florida water resources*, [online], v.1 (1). pp. 38-48
Available at:
http://www.lesico-cleantech.com/pdf/existing_and_emerging_concentrate_minimization.pdf
[Accessed 24th July 2014]

Squire. D. (2000) Reverse osmosis concentrate disposal in the UK, *Desalination*, [online], v.132 (3), December, pp.47-54
Available at: http://www.sciencedirect.com/science/article/pii/S0011916403002376
[Accessed 24th July 2014]

Saripallia. K, Sharmaa. M and Bryantb. S. (2000) Modeling injection well performance during deep-well injection of liquid wastes, *Hydrology,* [online], v.227 (4), January, pp.41-55
Available at: http://www.sciencedirect.com/science/article/pii/S002216949900164X
[Accessed 24th July 2014]

Skehan. S and Kwiatkowski. P (2000) Concentrate Disposal via injection wells-permitting and design Considerations, *Florida Water Resources*, [online], May, pp. 19-24
Available at: https://www.fwrj.com/articles3/0005.pdf
[Accessed 24th July 2014]

Spellman. F. (2016) *Reverse osmosis: A guide for the Nonengineering Professional*. USA. Taylor & Francis Group.

Saliba. L. (1996) *Guidelines for Authorizations for the Discharge of Liquid Wastes in the Mediterranean Sea. UNEP: California*. [online]. May.
Available at: https://books.google.co.uk/books/
[Accessed 24th July 2014]

Shiklomanov. I and Rodda. J. (2003) *World Water Resources at the Beginning of the Twenty-First Century:* Cambridge. United Kingdom: Cambridge University Press.

Senoussi. M. (2012) Interview by Ali Elhajaji. Sabha. Libya. 24th Jun 2012.

Sidon. A. (2013) Interview by Ali Elhajaji. Tripoli. Libya. 13 September 2013.

Salem. O. (2007) The great manmade river project: A partial solution to Libya's future water supply, *Water Resources Development*, [online], v. 8 (4), May, pp. 270-278
Available at: http://iahr.tandfonline.com/doi/abs/10.1080/07900629208722564
[Accessed 24th July 2015]

Safrai. I and Zask. A. (2008) Reverse osmosis desalination plants — marine environmentalist regulator point of view, *Journal of Desalination*, [online], v.220 (3), March, pp.72-84
Available at: http://www.sciencedirect.com/science/article/pii/S0011916407006066
[Accessed 24th July 2014]

Sandoval. J, Guirao. L and Ruiz. J. (2012) The effect of salinity increase on the photosynthesis, growth and survival of the Mediterranean seagrass Cymodocea nodosa, Estuarine, *Coastal and Shelf Science*, [online], v.115 (1), December, pp. 260–271
Available at: http://www.sciencedirect.com/science/article/pii/S0272771412003678
[Accessed 24th July 2014]

Sadhwania. J, Vezaa. J and Santanab. C. (2005) Case studies on environmental impact of seawater desalination, Journal of Desalination, [online], v.185 (3), November, pp. 1-8
Available at:-
http://www.sciencedirect.com/science/article/pii/S0011916405006041#
[Accessed 24th July 2014]

Stanley. S. (2006) Influence of seawater chemistry on biomineralization throughout Phanerozoic time: Paleontological and experimental evidence, *Journal of Palaeogeography, Palaeoclimatology, Palaeoecology*, [online], v.232 (4), March, pp.214-236,

Available at: http://www.sciencedirect.com/science/article/pii/S0031018205007182
[Accessed 24th July 2014]

Soror. T. (2009) Scale and Corrosion Prevention in Cooling Water Systems Part I: Calcium Carbonate, *The Open Corrosion Journal*, [online], v.2 (1), February, pp.45-50.
Available at: - http://benthamopen.com/contents/pdf/TOCORRJ/TOCORRJ-2-45.pdf
[Accessed 24th July 2014]

Student Watershed Research Project. (2014) *Introduction-alkalinity*, [online], pp 1-3
Available at: http://swrp.esr.pdx.edu/publications/manual/alkalinity_introduction.pdf
[Accessed 24th July 2014]

Saleem. M. (2011) Biofouling Management in the Cooling Circuit of a Power Industry Using Electrochemical Process, *General and Physical*, [online], v.33 (3), September, pp. 295-304
Available at: http://jcsp.org.pk/Search.aspx?s=Biofouling%20Management%20in%20the%20Cooling%20Circuit%20of%20a%20Power%20Industry%20Using%20Electrochemical%20Process
[Accessed 24th July 2014]

Saleem. M, Chakrabarti. M, Hasan. D, Islam. M, Yussof. R, Hajimolana. S, Hussain. M, Khan. G and Ali. B. (2012) On site Electrochemical Production of Sodium Hypochlorite Disinfectant for a power Plant Utilizing Seawater, *Electrochemical Science*. [online], vol.7 (1), May, pp.3929-3938,
Available at: http://www.electrochemsci.org/list12.htm#issue1
[Accessed 24th July 2014]

Sivasankar. B. (2008) *Engineering chemistry*, McGraw Hill, New Delhi. India

Shuttleworth. W. (1993). Evaporation, Chapter 4, in: Maidment. D.R (ed), Handbook of Hydrology. McGraw-Hill, New York

Shuttleworth. W. (2007) Putting the "vap" into evaporation, *Hydrology and Earth System Sciences*, [online], v.11 (1), January, pp.210-244
Available at: http://www.hydrol-earth-syst-sci.net/11/210/2007/
[Accessed 24th July 2015]

Tal. A. (2006) Seeking Sustainability: Israel's Evolving Water Management Strategy, *Science*, [online], v.313 (5790), August, pp.1081-1084
Available at: http://science.sciencemag.org/content/313/5790/1081
[Accessed 24th July 2017]

Tsiourtis. N. (2001) Desalination and the environment, *Desalination*, [online], v.141 (3), December, pp.223-236
Available at: http://www.sciencedirect.com/science/article/pii/S0011916401850013
[Accessed 24th July 2014]

Tsiourtis. N. (2001) Seawater desalination projects. The Cyprus experience, *Desalination*, [online], v.139 (3), September, pp.139-147
Available at: http://www.sciencedirect.com/science/article/pii/S0011916401003034
[Accessed 24th July 2014]

Tomaszewska. M. (2000) Membrane distillation—examples of applications in technology and environmental protection, *Environmental Studies*, [online], v.9 (1), January, pp.27-36
Available at: http://www.pjoes.com/pdf/9.1/27-36.pdf
[Accessed 24th July 2014]

Tripathi. N. (2016) The Disadvantages of Ion Exchange, [online]
Available at: http://sciencing.com/disadvantages-ion-exchange-8092882.html
[Accessed 24th July 2014]

Trieb. F. (2007) *Concentrating Solar Power for Seawater Desalination: Final Report, German Aerospace Centre (DLR) Section System Analysis and Technologies Assessment: Germany. DLR*. [online], November, pp.1-65
Available at: http://www.dlr.de/tt/aqua-csp
[Accessed 24th July 2015]

Tamtam. A, Gallagher. F, Olabi. A and Nahere. S. (2011) Higher education in Libya, system under stress, *Social and Behavioural Sciences*, [online], v.29 (1). January, pp.742-751
Available at:http://www.sciencedirect.com/science/article/pii/S1877042811027613
[Accessed 24th July 2015]

Torquemada. Y, Lizaso. J and Correa. J. (2005) Preliminary results of the monitoring of the brine discharge produced by the SWRO desalination plant of Alicante (SE Spain), *Journal of Desalination*, [online], v.182 (3), November, pp.395-402
Available at: http://www.sciencedirect.com/science/article/pii/S0011916405004546
[Accessed 24th July 2014]

Torquemada. Y and Lizaso. J. (2005) Effects of salinity on leaf growth and survival of the Mediterranean seagrass Posidonia oceanica (L.) Delile, *Experimental Marine Biology and Ecology*, [online], v.320 (5), June, pp.57-63
Available at: http://www.sciencedirect.com/science/article/pii/S0022098105000079
[Accessed 24th July 2014]

Torquemada. Y, Durako. M and Lizaso. J. (2005) Effects of salinity and possible interactions with temperature and pH on growth and photosynthesis of Halophila johnsonii Eiseman, *Marine Biology*, [online], v.148 (2), December, pp251-260
Available at:-
https://link.springer.com/article/10.1007/s00227-005-0075-5
[Accessed 24th July 2014]

Tonner. J. (2006) *An Environmental Literature Review and Position Paper for Reverse Osmosis Desalination Plant Discharges: Water Corporation of Western Australia, (Report No: 1890), Sydney*, [online], April, pp.1-38.
Available at: ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/BrinePanel/Resources/WaterConsultantsInt_ReverseOsmosisPaper.pdf
[Accessed 24th July 2014]

Tzen. E. (2014) *How Desalination growth affects the environment and energy demand*?, [online],
Available at: http://uest.ntua.gr/win4life/proceedings/papers/tzen.pdf
[Accessed 24th July 2014]

Tarnacki. K, Meneses. M, Melin. T, Van Medevoort. J and Jansen. A. (2012) Environmental assessment of desalination processes: Reverse osmosis and Memstill®, *Journal of Desalination*, [online], v.296 (1), June, pp.69-80
Available at:
http://www.sciencedirect.com/science/article/pii/S0011916412002093
[Accessed 24th July 2014]

Tabachnick. B and Fidell. L. (2013) Using Multivariate Statistics. 6th ed. USA: Prentice Hall.

Touchette. B. (2007) Seagrass-salinity interactions: Physiological mechanisms used by submersed marine angiosperms for a life at sea, *Journal of Experimental Marine Biology and Ecology*, [online], v.350 (2), November, pp. 194–215
Available at:
http://www.sciencedirect.com/science/article/pii/S0022098107003164#
[Accessed 24th July 2014]

Thangappan. R and Sampathkumaran. S. (2008) Electrochlorination system: a unique method of prevention of biofouling in seawater desalination, *Nuclear Desalination*. [online], v.3 (2).pp.135-143
available at:
http://www.inderscienceonline.com/doi/abs/10.1504/IJND.2008.020221
[Accessed 24th July 2014]

Thomas. D. (2009) Managing brine in inland regional recycling plants: *Beca Pty Ltd, Parramatta, NSW* [online], pp.1-6.
Available at:
http://www.beca.com/publications/technical_papers/~/media/publications/technical_papers/managing_brine_in_inland_regional_recycling_plants_2009.ashx

[Accessed 24th July 2015]

United Nations, (2001) *Water Desalination Technologies in the ESCWA Member Countries: Economic and social commission for western Asia*, [online], New York, July, pp.1-193
Available at: http://s3.amazonaws.com/zanran_storage/www.escwa.un.org/ContentPages/17952025.pdf
[Accessed 24th July 2014]

U.S. Department of the Interior Bureau of Reclamation (2009) *Bureau of Reclamation: Managing Water in the West: Brine-Concentrate Treatment and Disposal Options Report; Southern California Regional Brine-Concentrate Management Study – Phase I Lower Colorado Region:* [online], October, pp.1-89
Available at: http://www.usbr.gov/lc/socal/reports/brineconcentrate/6TreatmentandDisposal_part2.pdf
[Accessed 24th July 2014]

Uddin. S. (2014) Environmental Impacts of Desalination Activities in the Arabian Gulf, *Environmental Science and Development*, [online],v.5 (2), April, pp.114-117.
Available at: http://www.ijesd.org/index.php?m=content&c=index&a=show&catid=50&id=767
[Accessed 24th July 2014]

UNEP. (2014) *Mediterranean Action Plan (UNEP/MAP), State of the Mediterranean Marine and Coastal Environment*: Athens. Greece. [online].
Available at: http://www.undp.org/content/dam/turkey/docs/Publications/EnvSust/akdenizrapor.pdf
[Accessed 24th July 2014]

Viola. F, Sapiamo. M, Schembri. M, Brincat. C, Lopez. A, Toscano. A, Diamadopoulos. E, Charalambous. B, Molle. B, Zoumadakis. M, Armengol. A, Vich. M and Noto. M. (2014) The State of Water Resources in Major Mediterranean Islands, *Water Resources*, [online], v.41 (6). November, pp.639-648
Available at: https://link.springer.com/article/10.1134/S0097807814060207
[Accessed 24th July 2017]

Valero. F, Barceló. A and Arbós. R. (2011) Electrodialysis Technology - Theory and Applications, Desalination, Trends and Technologies, Schorr. M. (Ed), ISBN:978-953-307-311-8, InTech: Croatia, [online]
Available at: https://www.intechopen.com/books/desalination-trends-and-technologies/electrodialysis-technology-theory-and-applications
[Accessed 24th July 2014]

Voutchkov. N. (2010) *How much does seawater desalination cost? Water Globe Consulting, Texas Innovative Water,* [online],

Available at: http://www.twdb.texas.gov/innovativewater/events/tiw2010/
[Accessed 24th July 2014]

Voutchkov. N. (2014) Overview of seawater concentrate disposal alternatives, *Desalination,* [online], v.273 (1), June.pp.205-2019.
Available at: http://www.sciencedirect.com/science/article/pii/S0011916410007332
[Accessed 24th July 2014]

Verdier. F. (2011) *Mena regional water outlook: Part II: Desalination Using Renewable Energy: Task 1 – Desalination Potential*, [online], March, pp.1-47
Available at:-
http://www.dlr.de/tt/en/Portaldata/41/Resources/dokumente/institut/system/projects/MENA_REGIONAL_WATER_OUTLOOK.pdf
[Accessed 24th July 2014]

Voutchkov. N. (2013) *Desalination Engineering: Planning and Design*. McGraw-Hill, New York

Wittholz. M, O'Neill. B, Colby. C and Lewis. D. (2008) Estimating the cost of desalination plants using a cost database, *Desalination*, [online], v.229 (3), September, pp.10-20
Available at: http://www.sciencedirect.com/science/article/pii/S0011916408002683
[Accessed 24th July 2014]

World Health Organization. (1984) *Guidelines for drinking water quality Recommendations*, v. (I), Geneva, Switzerland: World Health Organization

Wade. N. (2001) Distillation plant development and cost update, *Desalination,* [online], v.136 (3), May, pp.3-12
Available at: http://www.sciencedirect.com/science/article/pii/S001191640100159X
[Accessed 24th July 2014]

Wang. L, Chen. J, Hung. Y and Shammas. N. (2011) *Membrane and Desalination Technologies,* London: Springer Science

WHO. (2007) *Desalination for Safe Water Supply: Guidance for the Health and Environmental Aspects Applicable to Desalination*, Geneva, [online],
Available at: http://www.who.int/water_sanitation_health/gdwqrevision/desalination.pdf
[Accessed 24th July 2014]

World Bank. (2012). Renewable Energy Desalination: An Emerging Solution to Close the Water Gap in the Middle East and North Africa. Washington, DC: World Bank. DOI: 10.1596/978-0-8213-8838-9. License: Creative Commons Attribution CC BY 3.0, [online]
Available at: http://elibrary.worldbank.org/doi/pdf/10.1596/978-0-8213-8838-9
[Accessed 24th July 2014]

Wade. N. (1993) Technical and economic evaluation of distillation and reverse osmosis desalination processes, *Desalination*, [online], v.93 (3), August, pp.343-363
Available at: http://www.sciencedirect.com/science/article/pii/0011916493801132 [Accessed 24th July 2014]

WHO. (2007) *Desalination for Safe Water Supply: Guidance for the Health and Environmental Aspects Applicable to Desalination, Public Health and the Environment World Health Organization Geneva*, [online], pp.1-161.
Available at: http://www.who.int/water_sanitation_health/gdwqrevision/desalination.pdf [Accessed 24th July 2014]

Wheida. E and Verhoeven. R. (2007) An alternative solution of the water shortage problem in Libya, *Water Resources Management*, [online], v.21 (6), June, pp.961-982
Available at: https://link.springer.com/article/10.1007/s11269-006-9067-6 [Accessed 24th July 2015]

Wheida. E and Verhoeven. R. (2006) Review and Assessment of Water Resources in Libya, *Journal of Water International*, [online], v.3 (3), Jan, pp. 295-309, [Online],
Available at: http://www.tandfonline.com/doi/abs/10.1080/02508060608691933 [Accessed 24th July 2015]

Williams. B, Onsman. A and Brown. T. (2010) Exploratory factor analysis: A five-step guide for novices, *Journal of Emergency Primary Health Care*, [online], v.8 (3), January, pp.1-13
Available at: http://ro.ecu.edu.au/cgi/viewcontent.cgi?article=1373&context=jephc, [Accessed 24th July 2014]

Walls. R, Canning. S, Lye. G, Givens. L, Garrett. C and Lancaster. J. (2013) *Analysis of Marine Ecology Monitoring Plan Data from the Robin offshore: Wind farm, Scotland (Operational Year 1), Report Nr: 1022189*, [online], January, pp.1-19
Available at: http://www.scotland.gov.uk/Resource/0041/00413017.pdf, [Accessed 24th July 2014]

Wildebranda. C, Gladea. H, Willa. S, Essigb. M, Riegerb. J, Büchnerc .K and Brodtc. G. (2007) Effects of process parameters and anti-scalants on scale formation in horizontal tube falling film evaporators, *Journal of Desalination*, [online], v.204 (3), February, pp.448-463
Available at: http://www.sciencedirect.com/science/article/pii/S001191640601349X [Accessed 24th July 2014]

World Health Organization (2005) *Desalination for Safe Water Supply, Guidance for the Health and Environmental Aspects Applicable to Desalination*, [online], pp.1-137,
Available at: http://www.who.int/water_sanitation_health/gdwqrevision/desalination.pdf
[Accessed 24th July 2014]

Xu. P, Cath. T, Robertson. A, Reinhard. M, Leckie. J and Drewes .J. (2013) Critical Review of Desalination Concentrate Management, Treatment and Beneficial Use, *Environmental Engineering Science*, [online], v.30 (8), August. Pp.502-514
Available at: http://online.liebertpub.com/doi/abs/10.1089/ees.2012.0348
[Accessed 24th July 2014]

Xevgenos. D, Vidalis. A, Moustakas. K, Malamis. D, Loizidou. M. (2015) Sustainable management of brine effluent from desalination plants: the SOL-BRINE system, *Desalination and Water Treatment*, [online], v.53 (12), July, pp. 3151–3160
Available at: http://www.tandfonline.com/doi/abs/10.1080/19443994.2014.933621
[Accessed 24th July 2014]

Xu. J, Ruan. G, Zou. L, Gao. C. (2010) Effect of chlorine and acid injection on hollow fiber RO for SWRO, *Desalination.* [online], v. 262 (3), November, pp.115-120
Available at: http://www.sciencedirect.com/science/article/pii/S0011916410003735
[Accessed 24th July 2014]

Younos. T and Tulou. K. (2005) Overview of Desalination Techniques, Contemporary water research and education, [online], v.1 (132), December, pp.3-10.
Available at: http://ucowr.com/files/Achieved_Journal_Issues/v132Overview%20of%20Desalination%20Techniques.pdf
[Accessed 24th July 2014]

Youssef. P, Dadah. R and Mahmoud. S. (2014) Comparative Analysis of Desalination Technologies, *Energy Procedia*, [online], v.61 (1), January, pp.2604-2607
Available at: http://www.sciencedirect.com/science/article/pii/S1876610214032871
[Accessed 24th July 2014]

Younos. T. (2005) Environmental Issues of Desalination, *Contemporary Water Research & Education*, [online], v.132 (1), pp.11-18
Available at: http://onlinelibrary.wiley.com/doi/10.1111/j.1936-704X.2005.mp132001003.x/full
[Accessed 24th July 2014]

Yolanda. T and Luis. S. (2006) Effects of salinity on growth and survival of Cymodocea nodosa (Ucria) Ascherson and Zostera noltii Hornemann, Biologia *Marina Mediterranean*, [online], v.13 (6), January, pp 46-47
Available at: http://rua.ua.es/dspace/handle/10045/6576?locale=en
[Accessed 24th July 2014]

Zander. A, Elimelech. M, Furukawa. D, Gleick. P, Herd. K, Jones. K, Rolchigo. P, Sethi. S, Tonner. J, Vaux. H, Weis. J and Wood. W. (2008) *Desalination: a National Perspective*. The National Academies Press, Washington. USA, [online]
Available at: https://www.nap.edu/catalog/12184/desalination-a-national-perspective
[Accessed 24th July 2014]

Zeleňáková. M, Purcz. P. Gargar. I and Hlavatá. H. (2014) Research of monthly precipitation trends in Libya and Slovakia: Recent Advances in Environmental Science and Geoscience. *Proceedings of the 2014 International Conference on Environmental Science and Geoscience (ESG '14)*, [online], Venice, Italy 15th -17th of March 15-17, pp. 46-50
Available at: http://www.inase.org/library/2014/venice/ENVIR.pdf#page=46
[Accessed 24th July 2015]

Appendixes